PEROVSKITE $CsPbBr_3$ NANOCRYSTALS WITH OLEIC LIGANDS GRAFTED ON ZnO SURFACES: DFT STUDY OF ELECTRONIC PROPERTIES

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Abstract

Semiconductor $CsPbBr_3$ (CPB) perovskite materials exhibit narrow band gap (about 2.5 eV) and possess very fast (hundreds of picoseconds) and strong free exciton luminescence (green at the nanoscale). CPB combination with ZnO microrods can further enhance photoluminescence. In this work the impact of ZnO polar and non-polar surface terminations on the properties of ZnO system with CPB nanocrystals passivated by oleic ligands is investigated. Calculations of structure and electronic properties by density functional theory (DFT) methods are compared on polar surfaces (Zn-face (0001), O-face $(000\bar{1})$), and non-polar surfaces ($(10\bar{1}0)$ and $(11\bar{2}0)$) before and after grafting CPB crystal with oleic ligands (OA, OAm). We find that on Zn-face ZnO surface the attachment of CPB with ligands causes increase of the band gap whereas on the other three ZnO surfaces the attachment of CPB with ligands caused the decrease of the band gap. The position of Fermi level with respect to HOMO and LUMO is also changing, indicating possible charge transfer and doping effects.

Keywords: Perovskite, ligands, ZnO surfaces, density functional theory

1. INTRODUCTION

Semiconductor CPB perovskite have been regarded as exciting materials in recent years for owing exciting structural, electronic and optical properties, low cast fabrication and high power conversion efficiency [1-3]. This unprecedentedly high power conversion efficiency has led towards high absorption coefficient in visible light range, high photoluminescence quantum yields, low rate of electron-hole pair recombination, high bipolar charge carrier mobility, tunable emission wavelength, balanced charge mobility (electron-hole), high carrier lifetimes, narrow full width at half maxima, and high diffusion lengths [4]. CPB is promising material for high-energy radiation detection and optoelectronic applications due to its large carrier diffusion length, high carrier mobility and photophysical properties [5]. Unfortunately, poor stability of CPB hindered its potential applications [6]. To improve the stability of CPB generally different ligands or coating are applied. The oleic ligands (OA, OAm) generate surface passivation, prevent aggregation, enhance dispersion that is useful to enhance the optical properties and most importantly they provide environmental protection to CPB crystals [6]. $CsPbBr_3$ can be produced by changing the ratio of Cs to Pb, and the required phase of the crystal can be controlled by using suitable surface ligands or antisolvent [7]. To synthesize pure $CsPbBr_3$ or $Cs_4PbBr_6/CsPbBr_3$ perovskite composites, ligand-assisted supersaturated recrystallization procedure is used. In this procedure, Oleic acid (OA) and oleylamine (OAm) ligands are added to achieve evolution from $CsPbBr_3$ and intense green light emissive Cs_4PbBr_6/ OA/OAm to Cs_4PbBr_6 [7]. By introducing impurities into perovskite materials and applying computational engineering the optical and electronic properties can be altered, making them a suitable choice for different applications including solar cells [8]. Various strategies are being implemented for surface passivation of CPB through ligand exchange, doping, silica shells and introducing polymer encapsulations to tweak properties for different applications [9].

Recently, zinc oxide (ZnO) has gained valuable attention in different electronic applications where its wide band gap 3.37 eV and superior semiconductor properties provide required advantages [10]. The band gap, antioxidant and antimicrobial properties of zinc oxide can be tailored by doping of different elements [11]. Further, the surface chemistry and chemical stability of ZnO offers a platform for various molecular interactions at molecular and atomic levels [12]. The transparency and availability of ZnO offers its applicability in real-word applications [10]. Direct and wide band gap, well known optical properties, low toxicity, high biocompatibility and luminescence property of ZnO defines it extremely useful in various biomedical, heating and sensing applications [13-15]. It is important to mention that the same material can form different structures on the ZnO substrates depending on the surface terminations and orientations of the surface dipoles [16]. Therefore, it is important to study the impact of ZnO surface terminations on the properties of ZnO system with semiconductor perovskite CPB-like nanocrystals accommodated with oleic ligands to understand the properties of ZnO/CPB nanocrystals. In the current study, we aimed to elucidate the electronic interaction and properties of four different polar and non-polar ZnO surface orientations with and without CPB nanocrystals containing oleic ligands by theoretical calculations.

2. MATERIALS AND METHODS

The interaction of ZnO surface facets with CPB nanocrystals with oleic-ligands at atomic level has been investigated by implementing DFT method in Quantum ATK software. For this purpose, polar surfaces (Zn-face (0001) and O-face $(000\bar{1})$) and non-polar surfaces ($(10\bar{1}0)$ and $(11\bar{2}0)$ facets) were considered separately interacting with CPB slab containing oleic ligands (OA, OAm). To study the impact of ZnO surface terminations on the properties of the system, only one typical CPB slab with one orientation and one arrangement of oleic ligands was used while only the ZnO surface orientations were changed.

For computation of electronic properties of the proposed model, Linear Combination of Atomic Orbital was used as basis function. In this basis function, the generalized gradient approximation and the Perdew–Burke–Ernzerhof exchange–correlation functional were utilized for calculations. The DFT calculations were performed for eleven structures: for three unit cells of ZnO, CPB and CPB with ligands as shown in **Figure 1(a, d, g)**, for four different facets of ZnO, and for four structures, in which ligands were attached with CPB crystals and CPB crystals were placed on ZnO facets.

The ZnO surfaces and CPB slabs were prepared using cleave function in Quantum ATK. Interface builder function available in Quantum ATK was applied to define the bonding between ZnO surfaces, CPB slab and oleic ligands by design. Further, the oleic ligands (OA, OAm) were placed vertically with respect to CPB slab. A vacuum of 20 Å was imposed along the Z-axis to interrupt the lattice periodicity which eventually avoid nonphysical interaction of the wave functions. All systems under consideration were assumed to be periodic in A and B direction. Further the boundary conditions, Neumann to the left and Dirichlet to right along the C direction of the system were applied.

All surfaces of ZnO, CPB slabs and oleic ligands (OA, OAm) were relaxed (optimized) to their minimum energy levels to obtain the stable configuration before merging them together to run the final optimization process. Band structures and density of states (DOS) were calculated for those structures. Changes in electronic properties of the system were analyzed.

3. RESULTS AND DISCUSSION

The resulting optimized ZnO and CPB structures are shown in **Figure 1**. **Figure 1(b)** represents the band structure of optimized ZnO unit cell. This ZnO unit cell exhibits the direct band gap of 1.02 eV. The Fermi level (E_F) at the center confirms the intrinsic behavior with a direct band gap [5]. Similarly, **Figure 1(e)** represents the band structure of optimized CPB unit cell. The optimized CPB unit cell has a direct band gap of 2.75 eV. The value for the band gap obtained in **Figure 1(b)** was verified by DOS analysis of ZnO unit cell and the exact

value of the band gap was calculated in **Figure 1(c)**. Similarly, the value of the band gap obtained for optimized CPB unit cell in **Figure 1(e)** was verified by DOS analysis in **Figure 1(f)**. The results obtained for the case of CPB unit cell are in good comparison to the literature [2]. We calculated the band gap for ZnO unit cell at 3.70 eV using also semi empirical approach (results not shown here) and that value is also close to the literature [5]. However, the semi empirical approach does not support the calculations for the combined ZnO/CPB system.

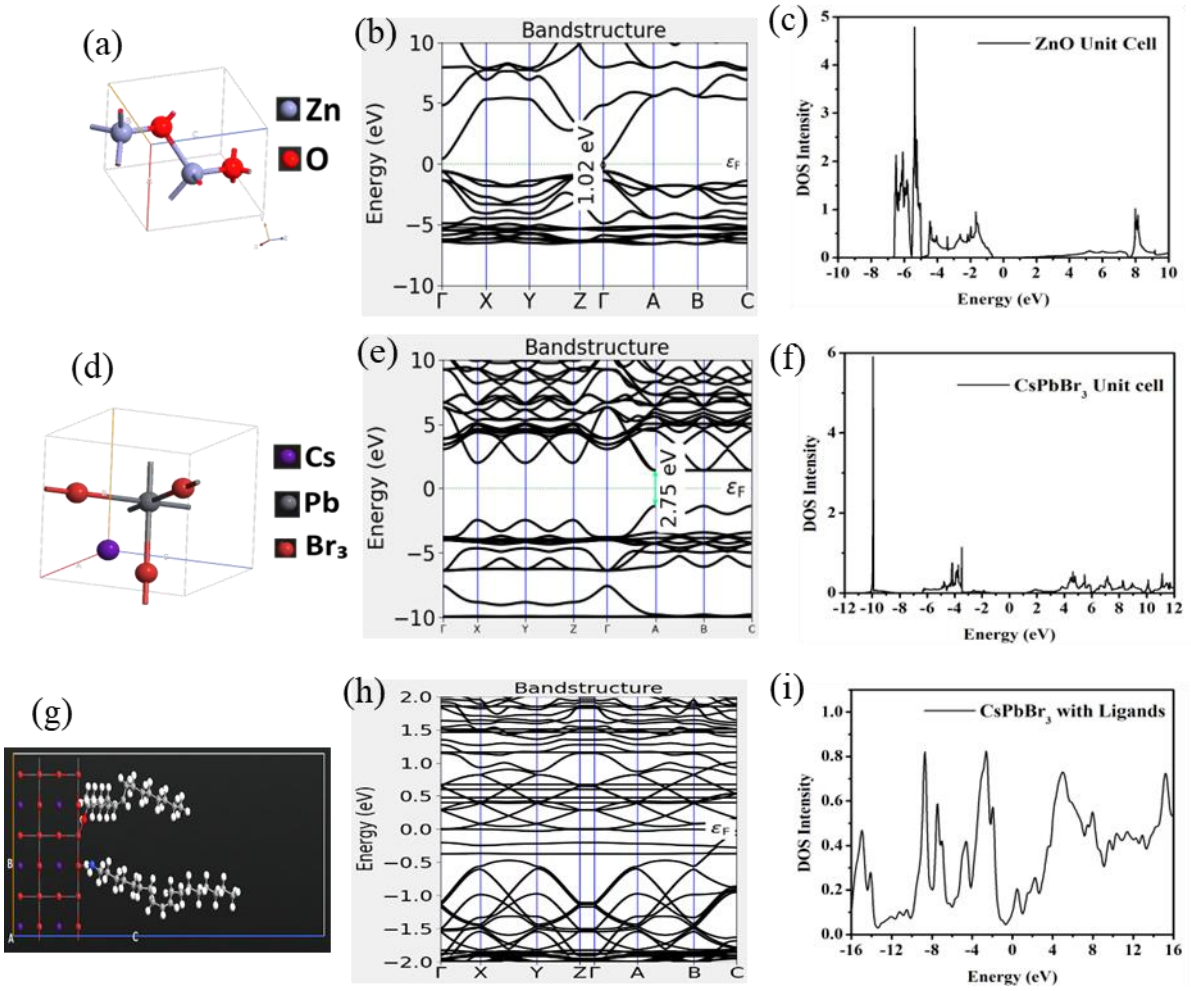

Figure 1 (a) Atomistic model, (b) band structure and (c) DOS analysis of optimized ZnO structure. (d) Atomistic model, (e) band structure and (f) DOS analysis of optimized CPB structure. (g) Atomistic model, (h) band structure and (i) DOS analysis of CPB with oleic ligands (OA/OAm). All calculated using DFT simulations.

Further, the interaction of CPB with oleic ligands (OA/OAm), as shown in **Figure 1(g)**, was considered and by band structure and DOS analysis the band gap of the system was found to be 0.0118 eV as shown in **Figure 1(h, i)**. These results show that when the oleic ligands (OA/OAm) are attached with CPB slab they significantly modify the electronic structure and band gap of CPB. When oleic ligands (OA/OAm) are attached with the surface of CPB possible local polarizations at the surface of oleic ligands (OA/ OAm) and CPB slab affect the electronic properties resulting in the modification of the band gap.

Figure 2 shows the optimized geometry of CPB slab containing oleic ligands (OA/OAm) and grafted on polar and non-polar ZnO slabs. Before further processing, the geometries in **Figure 2** were optimized to obtain the most stable configuration with the lowest energy states. **Figure 3** summarizes the results of simulations for

ZnO polar and non-polar facets ((0001), $(000\bar{1})$, $(10\bar{1}0)$ and $(11\bar{2}0)$) with and without CPB slab containing oleic ligands (OA/OAm). The DOS analysis was used to calculate the total unoccupied positions available for electrons at each energy level and assess the extent of contribution of each part of system towards the formation of HOMO and LUMO [17]. The area on the left with negative energy values represents the HOMO, while the region on the right with positive energy values represents the LUMO. The region of the band gap is present between these two regions in the center of the x-axis. The energy levels of HOMO and LUMO play a crucial role in the process of charge transfer between different parts of a system. A small energy gap between HOMO and LUMO facilitates the excitation and transfer of charge.

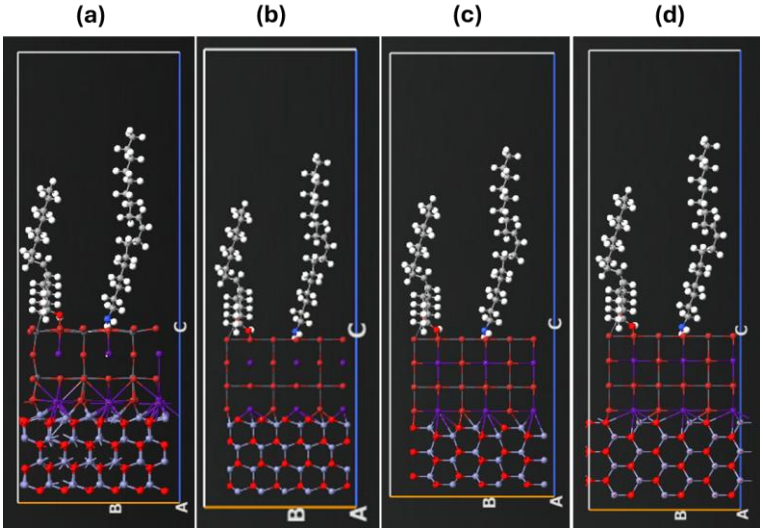

Figure 2 Optimized structural model of oleic ligands (OA, OAm) on CPB grafted on polar (a) Zn-face (0001), (b) O-face $(000\bar{1})$, and non-polar (c) $(10\bar{1}0)$ and (d) $(11\bar{2}0)$ ZnO facets.

Figure 3(a) shows that the band gap for the Zn-face polar slab (0001) is 1.06 eV. As a result of the interaction between the Zn-face polar slab (0001) with CPB slab containing oleic ligands (OA, OAm), the calculations show the value of the band gap increases and reaches 2.09 eV (**Figure 3(b)**). For the second case, the other polar face ZnO $(000\bar{1})$ was considered and after DOS analysis the band gap 1.78 eV was calculated (**Figure 3(c)**). When the CPB slab with oleic ligands was placed the results show the decrease in band gap from 1.78 eV to 0.25 eV (**Figure 3(d)**). Similarly, **Figure 3(e-f)** shows that the band gap for the case of ZnO $(10\bar{1}0)$ was modified from 2.29 eV to 1.98 eV and in **Figure 3(g-h)** for the case of ZnO $(11\bar{2}0)$ the band gap was modified from 4.01 eV to 1.99 eV.

It can be noticed that the placement of CPB slab with oleic ligands on the O-face ZnO resulted in decreasing the band gap significantly which can also result in smooth charge transfer between these moieties which is beneficial for better conductivity. Moreover, the results revealed that the attachment of CPB slab containing oleic ligands (OA, OAm) on Zn-face polar surface (0001) and slight increase of the bandgap is not improving the conductivity. Similar results were achieved using this similar approach on ZnO $(10\bar{1}0)$ and ZnO $(11\bar{2}0)$ facets.

The results in **Figure 3** demonstrate that it is possible to tune the band structure and DOS of the system. The electronic properties of polar and non-polar surfaces are modified in different manners [5]. In our case, all ZnO facets were tuned from their semiconductive nature to more conductive nature when ligands decorated CPB slab was placed on them except for the Zn-face ZnO (0001) surface where the wider band gap was observed. On the other hand, the $(000\bar{1})$ surface ZnO was tuned from 1.78 eV to 0.25 eV indicating drastic reduction in the band gap. These results conclude that the electronic properties of different ZnO facets can be tuned by introducing the CPB slabs passivated by oleic ligands (OA, OAm).

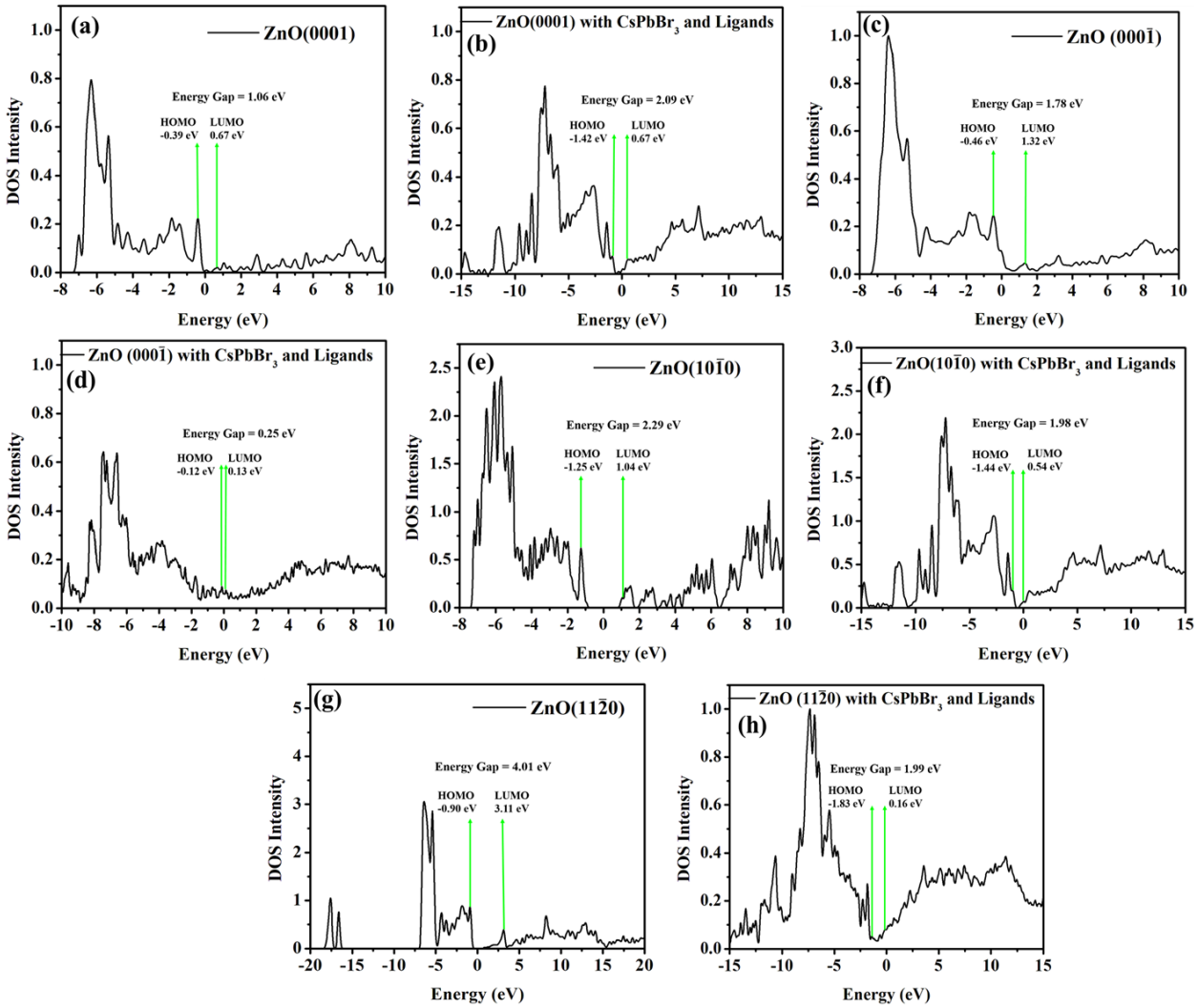

Figure 3 DOS analysis of polar (a) Zn-face (0001), (c) O-face $(000\bar{1})$, and non-polar (e) $(10\bar{1}0)$, (g) $(11\bar{2}0)$ ZnO facets standalone and after grafting CPB with oleic ligands (OA, OAm) on polar (b) Zn-face (0001), (d) O-face $(000\bar{1})$, and non-polar (f) $(10\bar{1}0)$, (h) $(11\bar{2}0)$ ZnO facets.

The flexible surface chemistry of CPB provides the option to dope them with different materials [18] for better conductivity for photovoltaic applications. Similarly, ZnO can be doped with different materials to modify its properties according to the requirements, i.e., Er-doped ZnO can be used for charge trapping process [19]. The luminescence and defects creation can be controlled by doping the ZnO nano and micro-rod with Er as well [20]. Similarly, molybdenum doped ZnO rods can be used to modify the luminescence and charge trapping phenomena of ZnO [21]. Our results show that merging CPB (with oleic ligands) and ZnO is other way to modify the electronic properties for different applications like scintillators or energy harvesting.

4. CONCLUSION

In this study the impact of ZnO surface orientation and atomic terminations on the properties of ZnO interface with semiconductor perovskite CPB nanocrystals passivated by common oleic ligands was investigated by theoretical DFT-based computations to understand the properties of ZnO/CPB interface. The results showed that the electronic properties of the ZnO/CPB system are modified in different ways depending on the ZnO surface orientation. On Zn-face ZnO surface the attachment of CPB with ligands caused the increase of the band gap from 1.06 eV to 2.09 eV. On the other three ZnO surfaces the attachment of CPB with ligands caused

the decrease of the band gap. Fermi level position and conductivity of the systems was also varied. Therefore, the electronic properties of ZnO/CPB nanocrystals can be tuned for practical applications in scintillators or energy harvesting. In particular the decrease in the energy band gap between and increase in conductivity can facilitate the excitation charge transfer in the ZnO/CPB system.

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