Research article

Evaluating the performance of Cs$_2$PtI$_6$–$x$Br$_x$ for photovoltaic and photocatalytic applications using first-principles study and SCAPS-1D simulation

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HIGHLIGHTS

- The geometrical structures, electronic, and optical properties of the mixed halide Cs$_2$PtI$_6$–Br$_x$ ($x = 0, 2, 4,$ and $6$) were investigated by DFT calculation.
- Cs$_2$PtI$_6$ material is suitable for single-junction solar cells, while other Br$^-$ doping are suitable for top cell in tandem solar cells.
- A device modeling of Cs$_2$PtI$_6$-based all-inorganic solar cells is provided using SCAPS-1D simulator.
- The results can guide more investigation and optimization of lead-free all-inorganic perovskite solar cells.

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ABSTRACT

All inorganic free-lead halide double perovskites are attractive materials in solar energy harvesting applications. In this study, density functional theory calculations have been used to predict the structures, band structures, and density of states of Cs$_2$PtI$_6$–Br$_x$ with ($x = 0, 2, 4,$ and $6$). The optical properties (reflectivity, refractive index, absorption, dielectric function, conductivity, and loss function) of these materials have been predicted and discussed. The band edges calculations showed that the Cs$_2$PtI$_6$–Br$_x$ may be an efficient visible-light photocatalyst for water splitting and CO$_2$ reduction. The calculated bandgap value of Cs$_2$PtI$_6$ exhibited a great match with the reported experimental values. It has been seen that increasing the doping content of Br$^-$ in Cs$_2$PtI$_6$–Br$_x$ ($x = 0, 2, 4,$ and $6$) increases the bandgaps from 1.4 eV to 2.6 eV and can be applied in single junction and tandem solar cells. Using Solar Cell Capacitance Simulator (SCAPS), a 1D device modelling has been performed on Cs$_2$PtI$_6$ inorganic lead-free solar cells. For the fully inorganic device, the effect of replacing organic hole transport materials (HTL) and electron transport materials (ETL) with inorganic ones is investigated while keeping high efficiencies and stabilities of solar cell devices. From the obtained results, it was found that WS$_2$ as ETL and Cu$_2$O as HTL were the most suitable materials compared to the others. Further investigation studies are performed on the effect of changing metal back contact work function, absorber layer thickness, doping density, and defect density on the power conversion efficiency (PCE) of the solar cell. The optimized suggested structure (FTO/WS$_2$/Cs$_2$PtI$_6$/Cu$_2$O/Carbon) obtained a PCE of 17.2% under AM1.5 solar illumination.

1. Introduction

The problem of climate change arises from burning fossil fuels which causes the problems of global warming and carbon dioxide (CO$_2$) evolutions [1]. Fossil fuel is a limited source of energy as it is depleting from the earth [2, 3]. These crises create a demand for research and development of alternative renewable sources of energy like solar energy harvesting. Solar energy is the cleanest, most abundant, and widely available source of energy. Solar energy is used in photovoltaic (PV) cells to produce electricity and can be conserved by a photocatalysis process to split water into hydrogen (energy vector), oxygen [4, 5], and CO$_2$ reduction through photo-chemical reactions [6, 7].

Perovskite materials are emerging in the field of solar energy harvesting because of their unique optical and electronic properties...
Many efforts are done for searching for visible light solar-driven water splitting photocatalysis [11, 12] and efficient photovoltaic devices [13, 14]. For photocatalysis applications, good photocatalysis for water splitting or CO2 reduction techniques should meet the requirement of (1) a suitable bandgap for absorption of the solar spectrum; (2) immediate electron-hole separation of the material; (3) high stability in aqueous medium against corrosion; (4) the redox potential of the material is suitable for H2 generation and CO2 reduction. Cs2PtI6 is also used as a photoanode for the photoelectrochemical (PEC) water oxidation process [15, 16] due to its stability even in an acidic or bases environment. In Jayanthan et al. [15], the heterojunction BIVO4/Cs2PtI6 is used and shows a high quality charge separation from BIVO4 to vacancy ordered Cs2PtI6. The achieved photocurrent density of the BIVO4/Cs2PtI6 junction is 0.92 mA/cm² at a potential of 250 mV. The bare BIVO4 gave 0.6 mA/cm² at a potential of 560 mV at 1.23 V (vs. RHE). In Hamdan et al. [16], the Cs2PtI6 was used as a photoanode for water oxidation in PEC cell. The Cs2PtI6 photoanode gave a photocurrent density of 0.8 mA/cm² with 12 h of stability. The material also used as an electrocatalyst for hydrogen production at pH~1 and stable for 6 h 1.23 V (vs. RHE).

For solar cell application, in comparison to conventional silicon solar cells, organic-lead halide perovskite solar cells show high performance. The perovskite solar cell PCE begin from 3.8% in 2009 [17] up to 25.5% in 2021 for single junction and 29.15% for perovskite/Si tandem two terminal cells [18]. Organic compounds are degradable which affects the stability of the solar cell. Another problem that limits the spreading of perovskite solar cells is the lead (Pb) element toxicity. Many efforts have been done to replace conventional organic (CH3NH3, CH(NH2)2) with inorganic (K+, Rb+, Cs+) [19, 20, 21, 22, 23, 24]. One of the high-efficiency candidates of inorganic solar cells is CsPbI3 [25, 26] which has an efficiency of around 20% [27] due to the slightly wide bandgap of CsPbI3 ~1.7 eV and the presence of lead. CsSnI3 has a band gap of ~1.3 eV which is ideal for capturing solar illumination [28] but suffers from low stability and the Sn2+ element oxidizes to Sn4+ forming the air-stable compound Cs2SnI6 [29]. This phenomenon attracts researchers to study the A2BX6 family perovskite to tackle the problem of instability and give alternatives for lead element. The drawback of CsSnI3 in solar cell fabrication is the lack of efficiency [30]. The maximum efficiency of CsSnI3 based solar cell is around 1.5% and 2.025% for mixed halide Cs2SnI4Br2 based solar cell [31]. One of the promising materials of A2BX6 family is CsPbI3. CsPbI3 is considered as a fully inorganic lead free double halide perovskite material. CsPbI3 crystallizes in the form of Fm-3m K2PtCl6 cubic structure form [32]. The stability of CsPbI3 material is up to 60 days in ambient conditions and 40 days in aqueous solution [33] and at high temperature [34]. It has a relatively high lifetime carrier of 2 µs and a low defect density of 2.5 × 1012 cm⁻³. Two prototypes of full device perovskite solar cell were fabricated with efficiencies of 10% and 13.88% respectively using ethylene diamine treatment [34]. Bromine (Br⁻) doping and substitution applied to many perovskites-based solar cells for tuning bandgap and increasing stability [35, 36, 37]. The Br⁻ doping affects the band gap of the structure and this in return allows the materials to be used in different photocatalysis water splitting and CO2 reduction applications.

One dimensional solar cell capacitance simulation program SCAPS-1D developed by Burgelman et al. in gent university [38, 39] considered as one-dimensional simulation tool that solves the continuity and Poisson equations for semiconductors. SCAPS-1D can model up to seven layers of solar cell device with the ability to modify the properties of every layer separately. The calculation results output can include current-voltage, capacitance-voltage, capacitance frequency, and quantum efficiency characteristics diagrams. The proper choice of ETL and HTL materials has a good impact on solar cell performance and stability.

The most used HTL material for perovskite solar cell is 2,2,7,7’-tetrakis-(N, N-di-4-methoxyphenylamino)-9,9-spirobifluorene (spiro-OMeTAD). Spiro-OMeTAD material suffers from lack of stability due to degradable organic elements besides it is expensive [40]. Other cuprous based HTL materials like cuprous oxide [41] and cuprous iodide [42] are integrated with PSC with high performance. Other HTL materials are investigated like MoO3 [43] for acquiring high performance, high stability, and low cost. ETL materials are important for the efficient electron collecting process to increase the PCE of solar cell. ETL material should maintain high electron mobility, chemical, and photostability. Another important feature is to be fabricated easily with perovskite materials. Indium gallium zinc oxide (IGZO) [44], zinc selenide (ZnSe) [45], and tungsten disulfide WS2 [46] attracted many researchers for their high conductivity and high mobility as a n-type semiconductor.

In this work, the structural, electronic, and optical properties of Br-doped Cs2PtI6 were performed by density functional theory (DFT) calculations. The suitability of these materials, as its possibility to be used as photocatalyst for water splitting and CO2 reduction processes was evaluated for the first time based on our best knowledge. The Cs2PtI6 material was simulated as the main absorber layer of a solar cell device. An investigation of different suitable inorganic HTL and ETL materials was done. The HTL materials are Cs2O3, CuI, MoO3 and spiro-OMeTAD organic HTL to compare with inorganic ones. The ETL materials are (IGZO, WS2, ZnSe, and CdS). The effect of the back contact work function on the performance of PSC is investigated. Furthermore, the change of thickness, doping, and defect density of Cs2PtI6 material are optimized for maximum PCE.

2. DFT study

2.1. Computational details

The structure of Cs2PtI6 has a face-centered cubic structure with a space group of Fm-3m (No. 225) [47]. The studied structures with Br⁻ doping were optimized using the Cambridge Serial Total Energy Package (CASTEP) program, which implements DFT [48]. The bandgap and the lattice parameter constants of Cs2PtI6 were calculated with local density approximation (LDA) [49] Perdew and Alex Zunger (CA) [50] - Perdew and Alex Zunger (PZ) [51] functional and the generalized gradient approximation (GGA) functionals (Perdew Burke-Ernzerhof (PBE) [52], revised PBE (RPBE) [53], revised PBE functional for solids (PBE0) [54], Wu-Cohen (WC) [55], and Perdew-Wang 91 (PW91) [56]), as well as the hybrid Heyd-Suess-Car-Enzerhof (HSE06) functional. Norm-conserving pseudopotential was used for the calculation of the interaction between the ionic core and valence electrons. The k-Monkhorst-Pack set was set to 3 × 3 × 3 along the Brillouin zone of the material structure. The cut-off energy is set to 480 eV for HSE06 calculations and 400 eV for the LDA/GGA functionals. The Broyden Fletcher-Goldfarb Shannon (BFGS) algorithm is used with convergence tolerance energy of 2 × 10⁻⁵ eV per atom. The convergence criteria of the interaction forces between atoms were set to 0.05 eV/Å, and the convergence criteria of maximum displacement of atoms are set to 0.002 Å. The optical properties of the Cs2PtI6 ·Br₋ were calculated by the RPBE method by energy calculations on the optimized unit cells obtained from the HSE06 calculations. The band gaps of the Cs2PtI6 ·Br₋ obtained from the HSE06 method were used in the optical (reflectivity, absorption, refractive index, dielectric function, conductivity, loss function) calculations using the scissors operator, as implemented in the CASTEP code.

The theoretical predictions of the bottom of the conduction band (Ecb) and the top of the valence band (EvB) edges of the Cs2PtI6 ·Br₋ (x = 0, 2, 4, and 6) were calculated according to Butler and Ginley [57]. The method mainly depends on Mullikens equations, which calculate the
values of electron negativity, electron affinity, $E_{VB}$ and $E_{CB}$. Mullikens defined the electron affinity of an atom, Eq. (1), as the arithmetic mean of atomic electron affinity $A_{f}$ tabulated in [58] and the first ionization energy $I_{1}$ tabulated in [59].

$$x_{atom}^{M} = \frac{1}{2} (A_{f} + I_{1})$$ (1)

For a compound with 3 elements $p$, $q$ and $r$ with number of atoms $l$, $m$ and respectively for each, [60, 61]. The electron negativity for a compound can be calculated using Eq. (2) as:

$$x_{compound}^{M} = \left( x_{p}^{M} : x_{q}^{M} : x_{r}^{M} \right)$$ (2)

Applying this equation to Cs$_2$PtI$_6$ material we obtain Eq. (3):

$$x_{Cs_{2}PtI_{6}}^{M} = \left( x_{Cs}^{M} : x_{Pt}^{M} : x_{I}^{M} \right)$$ (3)

Electron affinity $\chi$ of a compound can be calculated via Eq. (4) as:

$$\chi = x_{M} - \frac{1}{2} E_{g}$$ (4)

the theoretical predictions of $E_{CB}$ and $E_{VB}$ of the Cs$_2$PtI$_{6-x}$Br$_x$ ($x = 0, 2, 4$, and 6) were calculated using Eqs. (5) and (6) [62, 63], respectively.

$$E_{CB} = x_{atom} - E_{\text{free}} - 0.5 E_{g}$$ (5)

where $E_{\text{free}}$ is the energy of the free-electron on the hydrogen scale ($4.44 \pm 0.02$ eV), $E_{g}$ is the bandgap energy calculated from the HSE06 method. $\chi$ is the Mulliken's electronegativity of the semiconductor. The Mulliken's electronegativity ($\chi^{atom}$) of a neutral atom, is defined as the arithmetic mean of the atomic electron affinity and the first ionization energy:

$$E_{VB} = E_{CB} + E_{g}$$ (6)

2.2. Structure properties

The optimized crystal structures of Cs$_2$PtI$_{6-x}$Br$_x$ perovskites are shown in Figure 1. The pure structure is shown in Figure 1(a) Cs$_2$PtI$_6$, $x = 0$ and Figure 1(d) Cs$_2$PtBr$_6$, $x = 6$, respectively. The I to Br ratio in the structure Cs$_2$PtI$_{6-x}$Br$_x$ is represented by $x = 2$ for Cs$_2$PtI$_4$Br$_2$, Figure 1(b) and $x = 4$ for Cs$_2$PtI$_2$Br$_4$, Figure 1(c). As shown in Table 1, the bandgap of Cs$_2$PtI$_6$ is calculated using different DFT functionals. The GGA functionals used were PBE, RPBE, WC, PBESOL, and PW91 with resultant bandgap values of 1, 1.4, 0.8, 0.8, 1, and 0.5 eV, respectively, and LDA (CA-PZ) with a bandgap of 0.5 eV. These band gap values are not agreed with the experimental band gap (1.4 eV [34]), except for the RPBE functional. It is well known that the GGA/LDA functionals overestimate the band gap value, and probably the obtained band gap by the RPBE functional is just an artifact since it provides the worst band parameters among all tested functionals. The hybrid HSE06 has successfully predicted the experimental band gap (1.4 eV).

The reported experimental value of the lattice constant of Cs$_2$PtI$_6$ is 8.03 Å [32] which agrees with the HSE06 calculated lattice constant value as shown in Table 2 with an acceptable error of $\sim 1.6 \%$. The optimized lattice
constant of Cs$_2$PtBr$_6$ is 7.3 Å with an error of 3.2 % from the experimental measured value [64]. It is noticed that the Br$^-$ doping content increase reduces the lattice constant and increases the bandgap gradually.

### 2.3. Electronic properties

The calculated band structures of Cs$_2$PtI$_6$-$x$Br$_x$ are shown in Figure 2 using HSE06 functional. The calculated values of band gap of Cs$_2$PtI$_6$-$x$Br$_x$ are listed in Table 1. The calculated bandgap of Cs$_2$PtI$_6$ with HSE06 functional is 1.4 eV which agrees well with the experimental bandgap values of (1.4 eV [34] and 1.37 eV [33]). Till date, no experimental data are provided for the bandgap values of Cs$_2$PtI$_4$Br$_2$, Cs$_2$PtI$_2$Br$_4$, and Cs$_2$PtBr$_6$. The Cs$_2$PtI$_2$Br$_2$ has a bandgap of 1.6 eV, the Cs$_2$PtI$_4$Br$_2$ has a bandgap of 1.7 eV and Cs$_2$PtBr$_6$ has a bandgap of 2.6 eV.

Figure 3 shows the total density of states (DOS) and partial density of states (PDOS) of Cs$_2$PtI$_6$-$x$Br$_x$ using HSE06 functional. Fermi level position is dedicated by the dotted vertical red line at zero energy level. The PDOS of pure halide materials (Cs$_2$PtI$_6$ and Cs$_2$PtBr$_6$) show the dominance of I$^-$ 5p orbitals for the valence band maximum (VBM) and slight dominance of Cs$^+$ 6s and Pt-5d on the conduction band minimum (CBM), as shown in Figure 3(a,d). The PDOS for mixed halide materials (Cs$_2$PtI$_4$Br$_2$ and Cs$_2$PtI$_2$Br$_4$) show that the dominance in the VBM shared by I-5p and Br -4p orbitals, while Cs-6s and Pt-5d have slight dominance in the CBM, Figure 3(b,c).

### 2.4. Optical properties

The dielectric function is expressed as $\varepsilon_{\text{material}} = \varepsilon' - i \varepsilon''$ where $\varepsilon'$ is the real part of dielectric function and $\varepsilon''$ is the imaginary part. Figure 4(a) shows the real and imaginary part of the dielectric function versus the wavelength of the solar spectrum. The real part of the dielectric function of Cs$_2$PtI$_6$-$x$Br$_x$ is relatively high in the visible spectrum. The peaks of Cs$_2$PtI$_6$ are at $\lambda = 300$ nm and $\lambda = 550$ nm respectively. Increasing the Br$^-$ content causes a blue shift on the dielectric function.

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Table 1. The calculated lattice constant and bandgap of Cs$_2$PtI$_6$.

| Functional | GGA | LDA | HSE06 | Experimental |
|------------|-----|-----|-------|--------------|
|            | PBE | RPBE | WC    | PW91         | (CA-PZ)      |
| Bandgap (eV) | 1.4 | 0.8 | 0.8   | 1.4          | 1.4 [34]     |
|             | 0.5 | 1.4 | 0.5   | 1.4          | 1.37 [33]    |
| Lattice Å   | 8.3 | 8.9 | 8.06  | 8.05         | 8.2          |
|             | 7.8 | 7.8 | 7.9   | 8.03         | 8.03 [47]    |

Table 2. The calculated lattice parameter and bandgap of Cs$_2$PtI$_6$-$x$Br$_x$ using HSE06 functional versus experimental values.

| Material     | HSE06 | Experimental |
|--------------|-------|--------------|
| Lattice Å    | E_g (eV) | E_g (eV) |
| Cs$_2$PtI$_6$| 7.9   | 1.4          |
| Cs$_2$PtI$_4$Br$_2$ | 7.7   | 1.6          |
| Cs$_2$PtI$_2$Br$_4$ | 7.4   | 1.7          |
| Cs$_2$PtBr$_6$ | 7.3   | 2.6          |
| Cs$_2$PtI$_6$Br$_2$ | 7.9   | 8.03 [32]    |
| Cs$_2$PtI$_4$Br$_2$ | 7.7   | 1.4          |
| Cs$_2$PtI$_2$Br$_4$ | 7.4   | 1.7          |
| Cs$_2$PtBr$_6$ | 7.3   | 2.6          |

Figure 2. The band structures of (a) Cs$_2$PtI$_6$, (b) Cs$_2$PtI$_4$Br$_2$, (c) Cs$_2$PtI$_2$Br$_4$, and (d) Cs$_2$PtBr$_6$ by using the HSE06 functional.
function spectrum. The peak of the real part of the dielectric function of 
Cs$_2$PtBr$_6$ is at $\lambda = 350$ nm. The imaginary part of the dielectric function 
shows a blue shift increase with increasing Br$^-$ content. This means that 
the absorption of these materials can be tuned by Br$^-$ content doping. 
Figure 4(b) shows the real $n$ and imaginary $k$ part of the refractive index 
as a function of wavelength. The real refractive index of Cs$_2$PtI$_6$ increases 
gradually and then saturates for $>500$ nm with values of 2.5. Increasing 
Br$^-$ content lowers the $n$ values with a blue shift. Higher values of $n$ 
indicate a good absorption of the material to the incident spectrum. 
Extinction coefficient ($k$) indicates how the incident radiation attenuates 
through the material. Like the imaginary part of the dielectric function, 
increasing Br$^-$ content shows a blue shift in the $k$ values versus wave-
length. The higher values of $k$ of these materials are for $\lambda$ between 350 
and 450 nm in the middle of the spectrum which means high absorption 
of radiation by the materials in this region. The absorption coefficient ($\sigma$) 
of optical conductivity shows a red shift increase with Br$^-$ doping. The 
imaginary part of the optical conductivity shows a red shift increase with Br$^-$ 
doping.

2.5. Evaluation of the Cs$_2$PtI$_6$\textsubscript{x}Br$_x$ materials for photocatalysis and 
photovoltaic applications

2.5.1. Photocatalytic H$_2$, O$_2$ evolution, and CO$_2$ reduction process

Under solar illumination, the incident photons with energies higher 
than or equal to the bandgap of the semiconductor, the electrons in the 
valence band of the semiconductor excited to the conduction band 
leaving a positive hole. The photo-generated electron-hole pairs will 
move to the surface of the semiconductor and cause redox reactions. 
Figure S1 (Supplementary Information) shows the photocatalytic process 
under solar illumination. The determination of bandgap edges of the 
semiconductor is a key factor in the photocatalytic operation process. The 
bandgap edges positions define the thermodynamic limitations of the 
photocatalytic reaction caused by the photo-generated electron-hole pair of 
the semiconductor. The efficient photocatalytic water splitting semi-
conductor material should meet the criteria of (1) The semiconductor’s 
conduction band minimum should be more negative than the redox poten-
tial of H$^+$/H$_2$ (0 V vs NHE) and (2) the valence band maximum should 
be more positive than the potential edge of O$_2$/H$_2$O. These criteria apply 
to the CO$_2$ reduction photocatalytic process. The $E_{CB}$ and $E_{VB}$ values of

\[ \sigma_1 = \omega \varepsilon' \varepsilon_0 \]  
(7) 
\[ \sigma_2 = \omega \varepsilon' \varepsilon_0 \]  
(8) 

where $\sigma_1$ and $\sigma_2$ are real and imaginary part of optical conductivity, $\varepsilon_0$ 
is the dielectric constant of free space and $\omega$ is the angular frequency. The 
real part of optical conductivity spectrum shows a blue shift increase with 
Br$^-$ doping. The imaginary part of the optical conductivity shows a red 
shift increase with Br$^-$ doping.
Cs2PtI6, Cs2PtI2Br4 and Cs2PtBr6 are shown in Figure 5. It is noticed that the $E_{CB}$ values are smaller than 0 V (the redox potential of H2) for the materials and the $E_{VB}$ values are greater than 1.23 V (the potential of O2). Thus, the Cs2PtI6-xBrx materials will be suitable for photo-catalytic water splitting. For CO2 reduction process, it is shown that all the materials $E_{VB}$ are more negative than the CO2/CH4OH and CO2/CH4. This means that the materials may be suitable for CO2 reduction to produce CH4OH and CH4. The $E_{VB}$ level of Cs2PtI6 is at $-0.12$ V which means that the material may be suitable for CO2 reduction to HCHO. Cs2PtI2Br2 material also may reduce CO2 to HCHO. The estimation of electron negativity, electron affinity and band positions are shown in supplementary information Table S1.

2.5.2. Photovoltaic device

From the DFT study, it is concluded that, All the four materials are direct bandgap semiconductors. Direct bandgap semiconductors are
more efficient to be applied for solar cell devices than indirect band gap semiconductors. According to Shockley–Queisser limit [66], to maintain high power conversion efficiency of a single junction solar cell, the best band gap efficiency of a material should be in the range of 1.3–1.4 eV [67]. The Cs$_2$PtI$_6$ has a bandgap of 1.4 eV which is suitable for single junction perovskite solar cell.

3. Numerical analysis of all-inorganic perovskite Cs$_2$PtI$_6$ solar cell device using SCAPS-1D

To the best of our knowledge, there is no report on the numerical analysis of Cs$_2$PtI$_6$-based all-inorganic perovskite solar cells PSCs. Therefore, further studies are required to figure out the optimum combination of different materials to be used as various layers in the Cs$_2$PtI$_6$-based PSC. In this work, a detailed investigation of Cs$_2$PtI$_6$-based PSCs is conducted. First, the validity of the simulation was verified by comparing experimental results with the simulation results. Since there is much room for further performance enhancement, the effects of different parameters (ETL and HTL layers, back metal contact, acceptor carrier and defect density concentrations) on the cell performance are investigated. In addition to determining the optimum thickness of the Cs$_2$PtI$_6$ active layer. Finally, the optimum PSCs cell structure was elected using the appropriate layers regarding the results of this study.

3.1. The basic simulation parameters

Table S2 (sup. information) summarizes the physical parameters of the simulated Cs$_2$PtI$_6$ solar cell device. The working temperature of the device is assumed to be as the actual experimental conditions 298.15 K equivalent to regular room temperature. The series resistant Rs is set to be 14 (Ω.cm$^2$) and the illumination is based on reference air mass AM1.5 spectra. The range of wavelength of the spectra is set to be in the range of 300–900 nm. The Cs$_2$PtI$_6$ based solar cell device is modelled as separate different seven layers. The front contact is modelled as a flat band with surface recombination velocity of electrons and holes are $10^5$ cm/s and $10^3$ cm/s, respectively. The metal back contact is modelled using different materials with different work functions and surface recombination velocity of electrons and holes are set to $10^3$ cm/s and $10^5$ cm/s respectively. The simulated device structure consisted of fluorine-doped tin oxide (FTO) as front contact followed by an ETL, perovskite, HTL layers and a metal back contact, as shown in Figure S2 (a). The solar cell device layers are modelled with two embedded interface defect layers (IDL); one between ETL and Cs$_2$PtI$_6$ active layer and the other is the back IDL between Cs$_2$PtI$_6$ and HTL layer. The front and back IDLs are ultra-thin 5 nm layers with the same physical parameters of the absorber active layer and used to determine the effect of the interface recombination. The physical parameters of FTO, IDLs and Cs$_2$PtI$_6$ are listed in Table S3. Physical parameters of different HTL and ETL materials are shown in Tables S4 and S5, respectively [34, 43, 47, 68, 69, 70, 71, 72, 73, 74, 75]. Metal contacts work function are shown in Table S6 [76, 77, 78, 79, 80, 81]. The defect density $N_t$ can be calculated from the bulk lifetime model, Eq. (9).

$$N_t = \frac{1}{\sigma \tau V_{th}} \quad \text{(9)}$$

where the $V_{th}$ thermal velocity of electrons and holes is 107 cm/s. The capture cross section of electrons and holes $\sigma$ are estimated to be $2 \times 10^{-14}$ cm$^2$. The carrier lifetime $\tau$ value of Cs$_2$PtI$_6$ is $>2 \mu$s. The initial estimated value of $N_t$ is found to be $2.5 \times 10^{12}$ cm$^{-3}$, and the energetic distribution is assumed to be single.

Figure 6. Band gap alignment of Cs$_2$PtI$_6$ material with different ETLs and HTLs.

Figure 7. (a) J–V measurement and (b) QE curves for Cs$_2$PtI$_6$-based solar cells assembled with different HTL materials.
3.2. Model device verification

Firstly, the model was verified with previously published experimental data reported by Schwartz et al. [34]. The typical reference-cell structure is FTO/CdS/Cs2PtI6/Spiro-OMETAD/Carbon. The CdS and Spiro-OMETAD are the initial ETL and HTL materials, respectively. The resulted current density-voltage (J-V) characteristics diagram of the solar cell with structure FTO/CdS/Cs2PtI6/Spiro-OMETAD/Carbon show a short circuit current density (Jsc) of 20.1 mA/cm², open circuit voltage (Voc) of 1.12 V, power conversion efficiency (PCE) of 10.16 % and fill factor (FF) of 44%, as shown in Figure S2 (b). These results are in a good agreement with the experimental results (the values are Jsc = 20 mA/cm², Voc = 1.12 V, PCE = 10.06 % and FF = 41%) [34]. The difference between numerical and experimental values is in the acceptable range.

3.3. Bandgap alignment for ETL and HTL

The ETL and HTL materials should be chosen with suitable band edges to match the CBM and VBM of the active layers to obtain a high-efficiency solar cell. The proposed bandgap alignment schematic diagram for different ETL and HTL materials with respect to Cs2PtI6 active layer is shown in Figure 6. All the HTL materials' highest occupied molecular orbital (HOMO) levels aligned well with the valence band level of

| Structure | Jsc (mA/cm²) | Voc (volts) | FF % | PCE % |
|-----------|--------------|-------------|------|-------|
| FTO/CdS/Cs2PtI6/Spiro-OMETAD/C | 20.1 | 1.12 | 44 | 10.16 |
| FTO/CdS/Cs2PtI6/MoO3/C | 20.14 | 1.11 | 61 | 13.9 |
| FTO/CdS/Cs2PtI6/Cu2O/C | 20.4 | 1.1 | 62 | 14.2 |
| FTO/CdS/Cs2PtI6/CuI/C | 20.13 | 1.12 | 60 | 13.7 |

Figure 8. (a) J-V measurement and (b) QE curves for Cs2PtI6-based solar cells assembled with different ETL materials.

| Structure | Jsc (mA/cm²) | Voc (volts) | FF % | PCE % |
|-----------|--------------|-------------|------|-------|
| FTO/IGZO/Cs2PtI6/Cu2O/C | 22.2 | 1.13 | 59.2 | 14.8 |
| FTO/ZnSe/Cs2PtI6/Cu2O/C | 22.3 | 1.12 | 58 | 14.7 |
| FTO/WS2/Cs2PtI6/Cu2O/C | 23.4 | 1.13 | 58.5 | 15.4 |

Figure 9. (a) J-V characteristics and (b) PCE for (FTO/WS2/Cs2PtI6/Cu2O/metal back contact), with different metal back contacts.
Cs₂PtI₆ material and the ETL lowest unoccupied molecular orbital (LUMO) level aligned well with the conduction band of the Cs₂PtI₆ material. The CBM, VBM of used ETL and HTL materials are stated from previously published experimental and theoretical work research. In order to maintain high efficiency PSC the choice of ETL material should meet the criteria.

(i) The mobility of electrons should be high to maintain fast electron transport within the ETL.

(ii) CBM alignment with the active material Cs₂PtI₆

For HTL materials it should meet the criteria.

(i) High chemical stability to environmental conditions

(ii) The hole mobility is good enough for fast transfer of the holes to the electrode.

(iii) Blocking the transfer of electrons to the anode.

(iv) The highest occupies molecular orbital (HOMO) should be higher than the VBM of perovskite layer to ensure the process of photo-generated holes extraction.

3.4. Effect of HTL materials

The ETL layer was fixed to be CdS however, Spiro-OMeTAD was used as a reference HTL materials, in addition to other three different materials namely MoO₃, Cu₂O and CaI were simulated to study the effect of HTL layer properties on the solar cell performance. J-V characteristics diagram and QE measurements with different HTLs are shown in Figure 7(a,b), respectively. The Cu₂O HTL has high hole mobility which in turns gives high performance, the solar cell device using Cu₂O material has PCE values of 14.2%, Voc of 1.12 V, Jsc of 20.4 and FF of 62% as shown in Table 3. The QE values are high all over the spectrum as the assumption of zero reflection at each layer of the device for calculations simplicity. The QE spectrum shows negligible change with different HTL materials. The reason of this is because the HTL materials are placed in the back of the structure and their optical absorptions are not significant.

3.5. Effect of ETL materials on the cell performance

In this section the HTL layer was fixed to be Cu₂O, since it shows the best appropriate performance with Cs₂PtI₆ active layer, as discussed in the previous section (section 3.4). Regarding to the ETL material, three different promising materials are selected and simulated namely, indium gallium zinc oxide (IGZO), tungsten sulphide (WS₂) and zinc selenide (ZnSe). These materials are expected to show good performance as they have a good matching with Cs₂PtI₆ active layer as illustrated in the band alignment schematic diagram, Figure 6. Changing ETL material has a significant effect on the value of both Jsc and Voc. For this type of cells CdS ETL layer has found to have the lowest values of Jsc and Voc compared to other selected ETL materials. However, IGZO and ZnSe ETL layers have similar effect in the Cell performance as described in Figure 8(a). WS₂ ETL layer has a remarkable change over other ETL materials, and this may be due to WS₂ has high electron mobility value [46], the ability of absorbing wide range of solar light (E₉~1.8 eV) and the good band alignment with Cs₂PtI₆. The QE values are relatively high for all the simulated ETL materials, as we considered zero reflection of the solar cell layers for simplicity. The QE values are the highest using WS₂ as ETL compared to other materialsFigure 8(b). For Cs₂PtI₆-based cell using WS₂ as ETL layer has the best effect on the cell efficiency, Jsc of 23.4 mA/cm², Voc of 1.13 V, FF of 58.5% and PCE values of 15.4%, as shown in Table 4.

3.6. Effect of the back metal contact on the cell performance

The metal back contact effect on solar cell device performance is studied. The work functions of the selected back contact metals were ranged from 4.6 to 5.1 eV. The J-V characteristics as a function of metal work function values are presented in Figure 9(a). The J-V increased gradually with work function values increase from 4.6 eV to 5 eV. It is observed that the J-V curves are overlapped when the metal back contact work function equal 5 and 5.1 eV, and it can be explained by the consistency of the band structures of the back contact with Cu₂O HTL material which in turns allows better carriers transfer. In terms of PCE,
The simulated thicknesses ranged of PCE and less material usage. The optimized structure of absorber layer change in PCE. The optimized structure of perovskite solar cell can be simulated with different NA,Nt values. The PCE increases from the simulation study as: FTO/WS2/Cs2PtI6/Cu2O/Carbon with different Cs2PtI6.

3.7. Optimization of absorber layer thickness

The thickness of active layer has an important influence on the solar cell device performance. Larger thickness allows for more photo absorption of light; however, the diffusion length of carriers may cause recombination of electron-hole pairs and affect the PCE, therefore a thickness optimization of the absorber layer should be done. Figure 10 shows the effect of changing the thickness of the Cs2PtI6 active layer on the performance of the optimized device structure (FTO/WS2/Cs2PtI6/Cu2O/Carbon) perovskite solar cell. The simulated thicknesses ranged from 200 to 800 nm. From the J-V curves, increasing the thickness of the active layer lowers the Voc values and enhances the Jsc values as shown in Figure 10(a). Increasing the active layer thickness gradually has a good enhancement on the Jsc of the PSC solar cell. The impact of NA on PCE can be explained Eqs.(10) and (11). The increase of NA decreases the saturation current I0 and in turns increase Voc.

The optimized structure of Cs2PtI6 based perovskite solar cell can be assumed from the simulation study as: FTO/WS2/Cs2PtI6 (400 nm)/Cu2O/Carbon and is shown in Figure S3 (a). The doping acceptor concentration of Cs2PtI6 layer can be estimated to be $10^{12}$ cm$^{-3}$ and the best defect density concentration levels Nt of $1 \times 10^{12}$ cm$^{-3}$. Figure S3 (b) shows the J-V characteristics diagram of the solar cell structure FTO/WS2/Cs2PtI6 (400 nm)/Cu2O/Carbon. The device short circuit current density (Jsc) of 28.15 mA/cm$^2$, open circuit voltage (Voc) of 1.3 V, power conversion efficiency (PCE) of 22.4 % and fill factor (FF) of 61%.

4. Conclusion

The geometrical structures, electronic, and optical properties of the mixed-halide Cs2PtI6$_x$Br$_{6-x}$ (x = 0, 2, 4, and 6) were investigated by DFT calculation. The HSE06 functional has successfully predicted the bandgap values of Cs2PtI6. The bandgap values range from 1.4 to 2.6 eV.

The defect density results from the fabrication methods of perovskite solar cell based on one or two step spin on solution methods. Fewer defect density concentrations cause higher power conversion efficiencies of perovskite solar cell [82]. The higher values of defect density concentration in the material cause high recombination rates in the material which influences PCE. For these reasons, the effect of defect density concentration on PCE should be studied. According to Eq. (9), the decrease in Nt value leads to increase in carrier lifetime and diffusion length which will reduce the recombination rates in Cs2PtI6 material and increase the PCE of the cell. The impact of defect density of the Cs2PtI6 layer on the PCE is shown in Figure 11(b). With the appropriate control of the defect density concentration level, the PCE can exceed 17% with defect density of $1 \times 10^{12}$ cm$^{-3}$.

Figure 9(b) shows the change of PCE with different metal back contacts. It can be observed that the PCE enhanced with metal back contacts with work functions ranged from 4.6 eV to 5 eV. Meanwhile, for the work function of carbon material (5 eV) and noble Au (5.1 eV), there is only a slight change in PCE. The suggested metal back contact is carbon with work function of 5 eV as it is a cheap available material and achieve high PCE.

Figure 11 shows the effect of doping concentration NA and defect density Nt of absorber layer change in PCE. The higher values of defect density concentration levels Nt of 1

\begin{equation}
I_{sc} = \frac{A}{q} \left( \frac{D_{in}}{N_A} + \frac{D_p}{N_t} \right)
\end{equation}

\begin{equation}
V_{oc} = \frac{kT}{q} \ln \left( \frac{I_s}{I_0} + 1 \right)
\end{equation}
4.9 eV. The optimization is expanded to simulate different CsPbI₃ absorber thickness. According to simulation, device with 400 nm absorber layer thickness has the better PCE. The doping concentration of 10²⁰ cm⁻³ has high performance of the device. The smaller values of defect density are essential for high performance device. The device has the best performance with defect density concentration of 1 × 10¹⁷ cm⁻³. The best possible efficiency of 17.2% for FTO/WS₂/CsPbI₃ (400 nm)/Cu₂O/Carbon can be achieved. The results can guide for more investigation and optimization of lead free all inorganic perovskite solar cell.

Declarations

Author contribution statement

Hadeer H. AbdElAziz: Performed the experiments; Analyzed and interpreted the data; Wrote the paper. Mohamed Taha, Laila Saad: Conceived and designed the experiments; Analyzed and interpreted the data. Waleed M.A. El Rouby, M.H. Khedr: Contributed reagents, materials, analysis tools or data; Revised the paper.

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