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Electrode-induced impurities in tin halide perovskite solar cell material CsSnBr₃ from first principlesYuhang Liang¹, Xiangyuan Cui²✉, Feng Li¹, Catherine Stampfl¹, Simon P. Ringer¹ and Rongkun Zheng¹✉

All-inorganic lead-free CsSnBr₃ is attractive for applications in solar cells due to its nontoxicity and stability, but the device performance to date has been poor. Besides the intrinsic properties, impurities induced from electrodes may significantly influence the device performance. Here, we systematically studied the stability, transition energy levels, and diffusion of impurities from the most commonly used electrodes (*Au*, *Ag*, *Cu*, *graphite*, and *graphene*) in CsSnBr₃ based on density functional theory calculations. Our results reveal that, whereas *graphite* and *graphene* electrodes exhibit negligible influence on CsSnBr₃ due to the relatively high formation energies for carbon impurities in CsSnBr₃, atoms from the metal electrodes can effectively diffuse into CsSnBr₃ along interstice and form electrically active impurities in CsSnBr₃. In this case, a significant amount of donor interstitial impurities, such as Ag_i^+ , Cu_i^+ , and Au_i^+ , will be formed under *p*-type conditions, whereas the Sn-site substitutional acceptor impurities, namely Au_{Sn}^{2-} , Ag_{Sn}^{2-} , and Cu_{Sn}^{2-} , are the dominant impurities, especially under *n*-type conditions. In particular, except for Au_i^+ , all these major impurities from the metal electrodes act as nonradiative recombination centers in CsSnBr₃ and significantly degrade the device performance. Our work highlights the distinct behaviors of the electrode impurities in CsSnBr₃ and their influence on the related devices and provides valuable information for identifying suitable electrodes for optoelectronic applications.

npj Computational Materials (2021)7:63; <https://doi.org/10.1038/s41524-021-00533-5>

INTRODUCTION

Over the past few years, hybrid organic-inorganic halide perovskites have attracted overwhelming attention for applications in solar cells, photodetectors, and phototransistors^{1–4}, because of the outstanding optoelectronic properties and low cost. In particular, the power conversion efficiencies (PCE) of perovskite solar cells have reached over 25%^{5,6}. However, their large-scale deployment is restricted by the toxicity of lead and poor stability. All-inorganic lead-free perovskite CsSnBr₃ is regarded as an auspicious alternative due to its similar perovskite structure to Pb-based counterparts and competitive semiconductor characteristics, including a direct bandgap⁷, suitable bandgap size⁸, favorable charge-carrier effective masses⁹, and high thermal stability¹⁰.

So far, there have been many experimental reports^{11–15} on CsSnBr₃-based solar cells. Although the long-term stability was well demonstrated, the optimal PCE only reached 3.04%, far from 28% as predicted for single-junction cells by the Shockley-Queisser model theory¹⁶. Recently, we showed that intrinsic defects have a great impact on CsSnBr₃ and device performance¹⁷. Different from other halide perovskite materials with characteristic high defect tolerance^{18,19}, CsSnBr₃ is susceptible to defects. In particular, a high concentration of Sn and Cs vacancies are predicted to be electrically active and play a mixed role in affecting the optoelectronic properties. They also exhibit mobile properties, especially under illumination, and tend to accumulate at the contact near the electrode, causing an unfavorable screening-field effect for the device performance.

In turn, CsSnBr₃ may also be susceptible to impurities from electrodes, which may have an impact on the related device performance. Many optoelectronic devices, such as photodetectors, adopt an electrode-perovskite-electrode configuration, where electrodes are directly deposited on the perovskites as the back

contact for the devices. In usual solar cell configurations, although a hole transport layer (HTL) or electron transport layer (ETL) separates the electrode and CsSnBr₃, the organic HTL/ETL are particularly susceptible to the diffusion of electrode ions. Indeed, as found for the MAPbI₃ solar cell²⁰, the atoms of the *Au* electrode can diffuse across the HTL/ETL and cause contamination to the active layer. Recently HTL-free perovskite solar cells have gained momentum due to the high cost and low stability of organic HTL²¹. As such the “direct contact” device configuration facilitates the interaction between the electrode and active layer. Although most electrodes such as *Au* and *Ag* do not directly react with CsSnBr₃, the constituent atoms of the electrodes may migrate into CsSnBr₃ and be trapped at the interstices or intrinsic vacancies to form electrically active impurities²². These unintentional electrode impurities may influence device performance by introducing deep levels as non-radiative recombination centers, screening the built-in electric field, and so on. Indeed, the trihalide perovskite analog MAPbI₃ active layer has been previously demonstrated to be susceptible to electrode impurities^{23,24}.

In this work, we investigated the effects of common electrode impurities on CsSnBr₃ device performance by first-principles density functional theory (DFT) calculations. We studied the most widely used electrodes of *Au*, *Ag*, *Cu*, and C^{11,15,25–27} due to their relatively low resistivities²⁸ and suitable work functions for carrier extractions. For carbon electrodes²⁹, we considered *graphite* and *graphene*. The Fermi energy levels (−5.10 eV for *Au*, −4.26 eV for *Ag*, −4.65 eV for *Cu*, and −5.00 eV for C)³⁰ are compatibly located above the valence band maximum (VBM) and below the conduction band minimum (CBM) of CsSnBr₃ that were measured to be −5.2 eV and −3.4 eV, respectively³¹. Such electrodes can effectively promote the extraction of photogenerated carriers from active layers and hence are the promising candidates for CsSnBr₃ devices.

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Phenomenologically, the formation of electrode impurities can be regarded as that the constituent elements first decompose from the electrodes, then diffuse into the bulk of the active layers, and finally form impurities in thermal equilibrium. Correspondingly, such a behavior can be evaluated by the cohesive energy of electrodes, the thermal stabilities, and the kinetic barriers of impurities in CsSnBr_3 . To this end, we first calculated the cohesive energy for the electrodes to assess the tendency of decomposing and the impurity element provision. Then, we calculated the formation energies of all the possible electrode impurities and their diffusion barriers in CsSnBr_3 , to understand whether they can diffuse in CsSnBr_3 and cause impurity formation. Finally, we calculated the transition energy levels to assess the optoelectronic properties of these impurities. Our results demonstrate that the metal species from the electrodes can effectively diffuse and introduce electrically active impurities in the CsSnBr_3 active layer. For carbon species, it requires to overcome higher cohesive energies to escape from the electrodes and higher formation energies to cause impurities in CsSnBr_3 and thus will have less influence on the active layer. These appealing features make carbon-based electrodes stand out as promising electrodes for related optoelectronic applications.

RESULTS AND DISCUSSION

Cohesive energies of electrodes

The calculated cohesive energies of the considered electrodes, Au , Ag , and Cu in equilibrium face-centered cubic geometry (FCC), and C (*graphite*, *graphene*), are shown in Table 1. Our results are in good agreement with the previous studies^{32–34}. The metal electrodes exhibit relatively low cohesive energies of 2.93 eV, 2.41 eV, and 3.42 eV per atom for Au , Ag , and Cu , respectively. By comparison, carbon electrodes exhibit relatively high cohesive energies, while it does not significantly differ between *graphite* and *graphene*, with the values of 7.97 eV per atom and 7.96 eV per atom for *graphite* and *graphene*, respectively, indicating atomic carbon requires to overcome higher energy to escape from *graphite* or *graphene* electrodes to contaminate the active layer.

Band structure of CsSnBr_3

Before exploring the behaviors of the impurities in CsSnBr_3 , we study the band structure of bulk CsSnBr_3 , which is significantly sensitive to defective calculation, especially the transition energy levels. As shown in Fig. 1, CsSnBr_3 exhibits a direct bandgap between the CBM and VBM at the R-point in the Brillouin zone. Previous reports^{35–37} suggest that spin-orbit coupling (SOC) is important in lead halide perovskites due to the strong relativistic effects of the heavy Pb elements, which may be relevant for Sn-based perovskites. Therefore, we calculated the PBE band structures with and without SOC, as shown in Fig. 1a, b. It is interesting that, although the PBE calculation sizably underestimates the bandgap value, our PBE calculation in CsSnBr_3 without consideration of SOC predicts a value of 1.41 eV,

compared with that of 0.60 eV for PBE + SOC, and the experimental one, 1.75 eV¹³. This is because the incorporation of SOC shifts the conduction band down by ~0.8 eV, while the top of the valence band is almost unchanged. Similar behavior was also found in other trihalide perovskite counterparts^{38–40}. Also, the higher level hybrid functionals, Heyd-Scuseria-Ernzerhof (HSE) was performed for bandgap correction (Fig. 1c, d). In this case, HSE overestimates the bandgap to 1.97 eV, while we obtained the bandgap of 1.83 eV when considered spin-orbit coupling. Among the results, PBE and HSE+SOC can predict a closer bandgap with respect to experimental value with a slight difference. Considering that the hybrid functionals are computationally expensive, pure PBE calculations have been widely used to study defects in perovskites^{41–43}. In particular, the PBE results for defect formation energy²⁴ and diffusion barrier²³ do not significantly differ from those from HSE+SOC. Thus, in the present study, the defect formation energy and diffusion barrier were presented in the PBE values. For the energy transition levels that are sensitive to bandgap error, both PBE and HSE+SOC calculations were conducted.

Impurity Formation energies

To explore whether the electrode ions can introduce impurities to influence the properties of CsSnBr_3 , we first calculated the formation energies of the possible point impurities, including the interstitial impurities (Au_i , Ag_i , Cu_i , and C_i) and the substitutional impurities (Au_{Br} , Au_{Sn} , Au_{Cs} , Ag_{Br} , Ag_{Sn} , Ag_{Cs} , Cu_{Br} , Cu_{Sn} , Cu_{Cs} , C_{Br} , C_{Sn} , and C_{Cs}).

The calculated formation energies of different impurities in the neutral and charged states as a function of the Fermi level (E_f) are summarized in Fig. 2. The Fermi level depends on the electronic condition of the host material. For example, the hole-rich condition (*p*-type) moves the E_f close to the VBM, whereas the electron-rich condition (*n*-type) moves the E_f close to the CBM. Interestingly, as shown in Fig. 2a, we found that all the carbon electrode-induced impurities act as acceptors in CsSnBr_3 . Graphite is more stable than graphene by 0.01 eV/atom (Table 1) hence lower bulk chemical potential, consequently *graphite*-induced impurities exhibit slightly higher formation energy, indicating that CsSnBr_3 is more susceptible to *graphene* electrode than *graphite* electrode. They have relatively high formation energies under both Sn-rich and moderate conditions, compared with that of metal impurities, which may be attributed to the relatively weak binding of carbon atoms with CsSnBr_3 . In particular, under hole-rich conditions (*p*-type), carbon atoms are difficult to incorporate as impurities in CsSnBr_3 and will have a negligible influence on the active layer. When the host is in electron-rich (*n*-type) conditions, these impurities tend to be ionized by trapping the electrons and the formation energies decrease. In particular, the formation energies of the C_i^{3-} and $\text{C}_{\text{Br}}^{3-}$ impurities are relatively low under *n*-type conditions, and they become the major impurities of carbon electrodes.

In stark contrast to the carbon electrode, the metal electrodes can introduce impurities with much lower formation energies and hence higher concentrations in CsSnBr_3 . As shown in Fig. 2b, the Sn-related substitutional impurities serve as acceptors with the lowest formation energies. Particularly, under electron-rich conditions (*n*-type), the negative formation energies indicate a considerable amount of impurities will form in negative divalent states ($\text{Au}_{\text{Sn}}^{2-}$, $\text{Ag}_{\text{Sn}}^{2-}$, and $\text{Cu}_{\text{Sn}}^{2-}$). The reasons for this are twofold. On one hand, in agreement with the recent experiment¹⁴, our calculations predict that CsSnBr_3 is susceptible to Sn vacancies¹⁷. The high concentration of Sn vacancies facilitates the accommodation of these substitutional impurities. On the other hand, the metal elements compatibly substitute at the Sn-site of CsSnBr_3 with almost no structural distortion as shown in the optimized structures. In addition to the Sn-related substitutional impurities,

Table 1. Ground-state cohesive energy calculated using PBE for Au (FCC), Ag (FCC), Cu (FCC), and C (*graphite*, *graphene*), compared with the results of previous DFT studies.

System	Cohesive energy (eV/atom)	Reference (eV/atom)
Au (FCC)	2.93	3.05 ³²
Ag (FCC)	2.41	2.51 ³²
Cu (FCC)	3.42	3.32 ³²
C (<i>graphite</i>)	7.97	7.64 ³³
C (<i>graphene</i>)	7.96	7.40 ³⁴

Fig. 1 The band structures of bulk CsSnBr_3 . Calculated with the **a** PBE, achieving a bandgap of 1.41 eV, **b** PBE+SOC (0.60 eV), **c** HSE (1.97 eV), and **d** HSE+SOC (1.83 eV).

the interstitial impurities from the metal electrodes exhibit the second-lowest formation energies in CsSnBr_3 . In contrast, they act as donors and each metal element tends to donate an electron to the host to form monovalent impurities (Au_i^+ , Ag_i^+ , Cu_i^+), especially under hole-rich conditions (*p*-type). Moreover, the Br- and Cs-site substitutional impurities (Au_{Br} , Au_{Cs} , Ag_{Br} , Ag_{Cs} , Cu_{Br} , Cu_{Cs}) exhibit relatively high formation energies. Only under the *n*-type limit, would there be any appreciable concentrations of Ag_{Cs}^- , Au_{Cs}^- , and Au_{Br} impurities, but they are not the major impurities and will have little influence on the active layer. We noted that negative defect formation energies have been widely reported in halide perovskite systems^{44–47}. While the exact reason for these seemingly unphysical values from DFT supercell method is still unknown, it could be tentatively attributed to the well-known electron correlation and self-interaction errors associated with DFT^{48,49}.

Kinetic barriers

The static low formation energies of electrode impurities do not necessarily determine whether they have high concentrations in CsSnBr_3 because high kinetic barriers are likely to obstruct the migrations of the species from the electrodes into the active layer. Therefore, we next calculated the diffusion barriers to explore whether these low-formation-energy impurities can be formed and influence the bulk properties of CsSnBr_3 . As mentioned above, the acceptor impurities ($\text{Au}_{\text{Sn}}^{2-}$, $\text{Ag}_{\text{Sn}}^{2-}$, $\text{Cu}_{\text{Sn}}^{2-}$) are the dominant impurity with particularly low formation energies especially under electron-rich conditions (*n*-type), while the donor impurities (Au_i^+ , Ag_i^+ , Cu_i^+) are thermodynamically favorable in the active layer under hole-rich conditions (*p*-type). Thus, the diffusion of metal atoms from electrodes into the bulk of the active layer will have two possible mechanisms: hopping via Sn vacancies ($\text{Au}_{\text{Sn}}^{2-}$, $\text{Ag}_{\text{Sn}}^{2-}$,

$\text{Cu}_{\text{Sn}}^{2-}$) and along the interstices (Au_i^+ , Ag_i^+ , Cu_i^+). These six charged defects will be considered in our diffusion calculations.

For the diffusion of the class of Sn-related substitutional impurities, it requires the assistance of the hopping of the Sn vacancies, hence, we considered three possible paths as displayed in Fig. 3a. The P1 path represents that the metal element diffuses to the Sn-site in the proximity of the impurities ([100] direction). The P2 path is along the face diagonal of the square planar structure ([110] direction), and the P3 path is along the cubic diagonal of the cubic lattice ([111] direction). For the interstitial metal impurities, one diffusion path is considered in the highly symmetric cubic phase CsSnBr_3 .

As shown in Fig. 3b, all the Sn-related substitutional metal impurities have lower diffusion barriers along the P2 path than those along the P1 and P3 paths, indicating that they prefer to diffuse along the [110] direction, which is in agreement with our previous diffusion study of Sn vacancies¹⁷. As expected, the barrier energies of the substitutional impurities are substantially higher than that of Sn vacancy (0.27 eV). Among them, $\text{Au}_{\text{Sn}}^{2-}$ exhibits the highest diffusion barrier, up to 2.13 eV, which may be attributed to the heavier Au atom and the larger structural distortion during the impurity diffusion. To measure the distortions, we used the sizes of the Br–Sn–Br angle α (β) in the square planar structures, as displayed in Fig. 4. In all the initial/final states, the Br–Sn–Br angles α/β are 90°, in agreement with the perfect structure. When the impurities diffuse, the structures are distorted and the values of angle α/β exhibit significant changes. In the transition states, the model of $\text{Au}_{\text{Sn}}^{2-}$ exhibits the most distortion with the Br–Sn–Br angle α/β significantly shifted to 104.3°/102.3°, compared with 103.8°/98.6° for $\text{Cu}_{\text{Sn}}^{2-}$ and 103.1°/88.5° for $\text{Ag}_{\text{Sn}}^{2-}$. This is followed by $\text{Cu}_{\text{Sn}}^{2-}$ with a barrier of 1.48 eV, and then $\text{Ag}_{\text{Sn}}^{2-}$ also with a relatively

Fig. 2 Impurity formation energies. The calculated formation energies of **a** carbon (two different carbon sources are considered: *graphite* (dashed line) or *graphene* (solid line)), and **b** metal (*Au*, *Ag*, and *Cu*) impurities as a function of the Fermi level, E_f , under the *Sn-rich* and *Moderate* conditions.

high diffusion barrier of 1.28 eV. The low formation energies (Fig. 2b) and the high diffusion barriers indicate the metal atoms from the electrodes will be trapped at Sn vacancies near the contact and will be ionized. These impurities (Au_{Sn}^{2-} , Ag_{Sn}^{2-} , Cu_{Sn}^{2-}) will slowly diffuse into the bulk of $CsSnBr_3$ over time.

Compared to the substitutional impurities in *Sn* sites, our results show that the interstitial metal impurities (Au_i^+ , Ag_i^+ , Cu_i^+) have lower diffusion barriers in $CsSnBr_3$. Especially for Ag_i^+ , its diffusion barrier is only 0.28 eV, indicating the most favorable kinetic conditions. Besides impurity Ag_i^+ , the impurities Cu_i^+ and Au_i^+ also exhibit low diffusion barriers of 0.42 eV and 0.67 eV, respectively. These results are close to those found in the $MAPbI_3$ system with

the diffusion barriers of 0.27 eV, 0.42 eV, and 0.42 eV for Ag_i^+ , Cu_i^+ , and Au_i^+ , respectively²³. Together with the low formation energies (Fig. 2b), such low diffusion barriers (Fig. 3b) allow the metal ions from the electrodes to efficiently diffuse into $CsSnBr_3$ along the interstice and form interstitial impurities in the bulk of the active layer. As shown in Fig. 5a, all the metal interstitial impurities (Au_i^+ , Ag_i^+ , Cu_i^+) prefer to locate at the interstitial site of the *Sn-Br* square plane and take a distorted structure, especially for Cu_i^+ . This may be attributed to the Coulomb attraction between the positively charged metal elements and the negatively charged bromine ions. The diffusion behaviors of the interstitial impurities (Au_i^+ , Ag_i^+ , Cu_i^+) can be described as the impurities hopping out of one *Sn-Br*

Fig. 3 The diffusion of major impurities. **a** The diffusion paths for substitutional impurities ($M = Au, Ag, Cu$) in α -CsSnBr₃. The green spheres depict metal elements (Au, Ag, Cu), the red one Br , the gray one Sn , and the purple one Cs . The red bars stand for the main modes of diffusion (lowest barrier), and the pink ones for the less favorable modes. For the substitutional impurities (Au_{Sn}^{2-} , Ag_{Sn}^{2-} , and Cu_{Sn}^{2-}), P1, P2, and P3 represent the diffusion directions of [100], [110], and [111], respectively.

Fig. 4 The diffusion of Sn-site substitutional impurities. The main modes of diffusion for impurities Ag_{Sn}^{2-} , Cu_{Sn}^{2-} , and Au_{Sn}^{2-} , where the initial, transition, and final states are on the left, middle, and right, respectively. The sizes of the $Br-Sn-Br$ angle α (β) in the square planar structures are used to measure the distortion of the structures. The spheres with different colors represent the different elements, yellow-Au, silvery-Ag, pink-Cu, red-Br, and gray-Sn.

plane and diffusing to the interstitial site on another $Sn-Br$ plane. Interestingly, as displayed in Fig. 5b–d, the diffusion path involves a meta-stable state where the metal species is located at the middle site between the initial $Sn-Br$ plane and final $Sn-Br$ plane without binding with any bromine ions, resulting in multiple kinetic barriers. The highest one is regarded as the diffusion barrier for the corresponding impurities, as summarized in Fig. 3b.

The metal ions exhibit particularly mobile properties within the interstices of CsSnBr₃. Our previous results¹⁷ revealed that the Sn vacancy is of high concentration in CsSnBr₃. One may envisage that the metal ions may penetrate CsSnBr₃ along the interstice, and then fill the Sn vacancies to form substitutional impurities in the bulk of the active layer. To support this hypothesis, we calculated the energy barriers for these processes, and the results

Fig. 5 | The diffusion of interstitial impurities. **a** Three structural motifs in the ground state for the interstitial impurities of Au_i^+ , Ag_i^+ , and Cu_i^+ on the Sn-Br square plane of α - $CsSnBr_3$. **b**, **c**, and **d** are the potential energy evolutions along the diffusion paths for impurities Ag_i^+ , Cu_i^+ , and Au_i^+ , respectively, in which the insets show the atomic structures of the corresponding NEB images.

are summarized in Fig. 6. In this case, the energy barrier is the diffusion barrier for the action that an interstitial metal ion M_i^+ hops and fills a neighboring Sn vacancy V_{Sn}^{2-} ($M_i^+ + V_{Sn}^{2-} \rightarrow M_{Sn}^{2-}$). Indeed, as shown in Fig. 6, all these processes are exothermic and the calculated barrier energies are only 0.10, 0.23 eV, and 0.32 eV, respectively, for Ag^+ , Cu^+ , and Au^+ , which indicates that the metal interstitial impurities tend to fill Sn vacancies and form the Sn-site substitutional impurities. Moreover, in contrast to the relatively high diffusion barriers of hopping through Sn sites, the metal species of impurities Ag_{Sn} , Cu_{Sn} and Au_{Sn} are mainly provided by the interstitial impurities diffused from the contact.

Charge transition levels

From the aforementioned results, the metal species from the electrodes can effectively diffuse along with the interstice and form the impurities in the bulk of the active layer. In particular, the

Sn-site substitutional acceptor impurities (Au_{Sn}^{2-} , Ag_{Sn}^{2-} , Cu_{Sn}^{2-}) are dominant, especially for *n*-type $CsSnBr_3$, while the interstitial donor impurities (Au_i^+ , Ag_i^+ , Cu_i^+) are also expected to exist with substantial concentrations in $CsSnBr_3$ under hole-rich conditions (*p*-type). Also, impurities C_i and C_{Br} are the major impurities induced by carbon-related electrodes (*graphite* and *graphene*). To understand whether these major electrode impurities can influence the optoelectronic properties of $CsSnBr_3$, we calculated the transition energy levels. For the minor impurities, due to the relatively high formation energies and less significant role in device performance, they will not be presented for a detailed discussion. It is well known that the transition energy level calculation is particularly sensitive to bandgap error. To obtain a more reliable value, we performed both PBE and HSE+SOC for this section, in which HSE+SOC calculation was based on the optimized structure of PBE level²⁴. In contrast to those outside the band edges, the

Fig. 6 Schematic of interstitials filling Sn vacancies. The energy profile of the interstitial metal ion ($M = \text{Au}, \text{Ag}, \text{and Cu}$) migration to the neighboring Sn vacancy. The inset is the schematic of the process, where the green spheres are depicted for metal elements ($\text{Au}, \text{Ag}, \text{Cu}$), the red ones for Br , and the gray ones for Sn .

Fig. 7 Impurity charge transition levels. The calculated transition energy levels within the bandgap for the major electrode impurities in $\alpha\text{-CsSnBr}_3$. The empty circles denote donors, and filled circles for acceptors.

transition energy levels within the bandgap are important for the optoelectronic property of the host and related device performance. As shown in Fig. 7, it is noticeable that PBE exhibits a qualitatively similar result to HSE+SOC, while the level values obtained by these two methods exhibit variations, which can be attributed to the different bandgap predictions by PBE and HSE+SOC. Moreover, due to a slight underestimation (1.41 eV) of PBE and overestimation (1.83 eV) of HSE+SOC compared with the experimental result (1.75 eV), we expect that the true level to be located between the values of PBE and HSE+SOC.

As shown in Fig. 7, as the major impurities induced from Ag electrodes, both results imply that Ag_{Sn} and Ag_i introduce deep energy levels inside the bandgap, which serves as nonradiative recombination centers causing energy loss and hence has a detrimental effect on the carrier transport in CsSnBr_3 . Similarly, for Cu electrodes, both Cu_{Sn} and Cu_i can trap electrons and holes at the middle of the bandgap, indicating that Cu electrode-induced impurities jeopardize the device performance as well. For the two Au-related impurities Au_i and Au_{Sn} , both PBE and HSE+SOC results show that the energy levels $\mathcal{E}(1+/0)$ of Au_i is below the VBM while $\mathcal{E}(2+/1+)$ is above the CBM so that it will be stable only at +1 state yet harmless to CsSnBr_3 . In contrast, the deep energy level introduced by Au_{Sn} makes the Au electrode detrimental to the active layer. Thus, it is obvious that when the host is under hole-rich conditions (p -type), the Au electrode has less influence and is preferable for devices. When under electron-rich conditions

(n -type), all the metal electrodes can significantly degrade the device performance by giving rise to deep energy level impurities ($\text{Au}_{\text{Sn}}^{2-}$, $\text{Ag}_{\text{Sn}}^{2-}$, $\text{Cu}_{\text{Sn}}^{2-}$). In this case, the shift of the growth conditions for the host to Sn-rich conditions will suppress the formation of these substitutional impurities, and help mitigate device performance deficiency. Moreover, in the case of carbon-based electrodes, in spite of the difference in the formation energies, the impurities from *graphite* and *graphene* exhibit the same transition energy levels. In particular, C_i and C_{Br} are the major impurities of carbon electrodes and can induce deep energy level $\mathcal{E}(1-/2-)$ of 0.90 eV (1.23 eV) and 0.57 eV (1.12 eV) within the bandgap based on PBE (HSE+SOC) calculation. Compared to the metal counterparts, these impurities exhibit relatively high formation energies, thus will have less influence on the active layer and related optoelectronic devices. Furthermore, the merits²⁷ of low-cost, high electrical conductivity, chemical stability, and modifiability enable the carbon materials as the promising electrodes for CsSnBr_3 -based optoelectronic applications.

In conclusion, based on extensive first-principles calculations, we systematically studied the behavior of the impurities from commonly used electrodes ($\text{Au}, \text{Ag}, \text{Cu}, \text{graphite}$, and *graphene*) in the bulk of the CsSnBr_3 and the possible influence they have on the optoelectronic device performance. For carbon-related electrodes, both *graphite* and *graphene* exhibit relatively high cohesive energy, and the related impurities have high formation energies. Within the system, the carbon species tend to be in the form of interstitial and substitutional impurities (C_i^{3-} and $\text{C}_{\text{Br}}^{3-}$) under the n -type limit, which can introduce deep energy levels in the bandgap, yet with limited concentrations. Thus, *graphene* and *graphite* stand out as promising electrodes for related optoelectronic applications. By comparison, the decomposition of metal electrodes will provide a considerable amount of metal atoms that can efficiently diffuse into CsSnBr_3 along the interstice and form various types of impurities. Among them, the Sn-site substitutional impurities ($\text{Au}_{\text{Sn}}^{2-}$, $\text{Ag}_{\text{Sn}}^{2-}$, and $\text{Cu}_{\text{Sn}}^{2-}$) are the dominant defects, especially for n -type CsSnBr_3 , in which it serves as an acceptor. When the host is under the hole-rich conditions (p -type), a significant amount of interstitial impurities (Au_i^+ , Ag_i^+ , and Cu_i^+) also will be formed in the active layer and serve as donors. Except for Au_i^+ , all these major impurities can introduce deep energy levels as nonradiative recombination centers to significantly cause device performance loss. Although the Sn-rich growth condition for CsSnBr_3 will mitigate this effect, more care should be taken to prevent the metal species from contaminating the active layer in related optoelectronic devices.

METHODS

First-principle calculations

Our calculations were based on density functional theory (DFT) as implemented in the Vienna ab initio simulation package (VASP) code⁵⁰. The projector-augmented-plane-wave method was used to describe the core–valence interaction⁵¹. The cut-off energy for basis functions was 400 eV. The Perdew–Burke–Ernzerhof (PBE)⁵² form of the generalized gradient approximation (GGA) and the higher level hybrid functional, Heyd–Scuseria–Ernzerhof (HSE)⁵³ were employed to describe the exchange and correlation functional theory. The HSE calculation was performed based on the optimized structure of PBE level^{23,24}. The effect of spin-orbit coupling was considered. A $2 \times 2 \times 2$ reciprocal space k -point mesh was used for the sampling of the Brillouin zone. CsSnBr_3 is in the cubic phase at room temperature⁷, so we used the cubic phase $\alpha\text{-CsSnBr}_3$ for our calculations. We employed a $3 \times 3 \times 3$ 135-atom supercell for the impurity simulations. Convergence test using a $4 \times 4 \times 3$ 240-atom supercell for the two energetically favorable defects, $\text{Ag}_{\text{Sn}}^{2-}$ and Au_i^+ , reveals that the formation energy deviations between the 135- and 240-atom supercells are less than 0.02 eV. All the structures were fully relaxed until all the forces on the atoms are below 0.01 eV/Å. For charged defects calculations, extra electrons (holes) together with uniform compensating charges were added to the supercell.

Cohesive energies

The cohesive energy is calculated as,

$$E_{\text{coh}} = (NE_{\text{atom}} - E_{\text{cell}})/N \quad (1)$$

Here, the E_{cell} stands for the total energy of the unit cell of electrode geometry that contains N atoms. The E_{atom} is the spin-polarized total energy of a single isolated atom of the corresponding electrode material.

Defect formation energies

To assess the thermal stabilities of the electrode impurities in CsSnBr_3 , we calculated the formation energies. For an impurity a ionized to a charge state q , its formation energy $\Delta H_f(a, q)$ is described as⁵⁴

$$\Delta H_f(a, q) = E(a, q) - E(\text{host}) - \sum n_i(\mu_i + \Delta\mu_i) + q(E_f + E(\text{VBM}) + \Delta V) \quad (2)$$

where the $E(a, q)$ and $E(\text{host})$ are the total energies of the supercells with and without impurities, respectively. The n_i is the difference in the number of atoms in these supercells. The E_f is the energy of the Fermi level relative to the VBM, and $E(\text{VBM})$ is the valence band maximum energy. The correction term, ΔV , was introduced for the alignment of potentials in different impurity supercells, which will have a bulklike environment with that in the bulk. The μ_i is the bulk chemical potential of atoms corresponding to the most stable elemental phase. In particular, the chemical potential of C atom will be calculated by the phases of *graphite* and *graphene*. The relative chemical potentials, $\Delta\mu_i$, of component atoms (Cs, Sn, and Br) should be restricted in the green region (see Supplementary Fig. 1), which has been demonstrated from our previous CsSnBr_3 defect study¹⁷. For the impurity atoms, Au, Ag, Cu, and C, we assumed they are in equilibrium with the “electrode-rich condition” for CsSnBr_3 near the electrodes, and thus set their relative chemical potentials $\Delta\mu_i$ to be zero. Moreover, for reference purposes, we chose two vastly different chemical conditions for our study. They are the Sn-rich and moderate conditions corresponding to the point A ($\Delta\mu_{\text{Cs}} = -2.66$ eV, $\Delta\mu_{\text{Sn}} = 0$ eV, $\Delta\mu_{\text{Br}} = -1.18$ eV) and the point B ($\Delta\mu_{\text{Cs}} = -3.29$ eV, $\Delta\mu_{\text{Sn}} = -1.23$ eV, $\Delta\mu_{\text{Br}} = -0.56$ eV) in Supplementary Fig. 1, respectively.

Diffusion barriers

The impurity diffusion barrier was calculated using the nudged elastic band method in conjunction with the climbing image method^{55–57}, as implemented using the VTST (VASP Transition State Tool) extension of the VASP code, which enables the determination of the minimum energy path between two energetically stable endpoints. For each pathway, we calculated six images intercalated between the relaxed initial state and final state for searching transition state. For the diffusion pathways with multiple kinetic barriers, the highest one is regarded as the diffusion barrier.

Transition energy levels

The transition energy levels $\varepsilon(q/q')$ of impurities are decided by the position of the Fermi level, where the formation energy of the impurity with the charge state q is equal to that of the charge state q' . Thus, it can be described by⁵⁴:

$$\varepsilon(q/q') = [E(a, q) - E(a, q') - (q - q')(E(\text{VBM}) + \Delta V)]/(q - q') \quad (3)$$

DATA AVAILABILITY

All data needed to evaluate the conclusions in the paper are present in the paper and the Supplementary Materials. Additional data for this study are available from the corresponding author upon reasonable request.

Received: 9 February 2021; Accepted: 7 April 2021;

Published online: 06 May 2021

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ACKNOWLEDGEMENTS

This research was undertaken with the assistance and resources from the National Computational Infrastructure (NCI Australia), an NCRIS enabled capability supported by the Australian Government. We acknowledge the support provided by the Sydney Informatics Hub at the University of Sydney in accessing these resources. This work is partially supported by the Australian Research Council (DE180100167).

AUTHOR CONTRIBUTIONS

Y.L., X.C., and R.Z. conceived the idea. Y.L., X.C., and R.Z. performed the DFT computations. All authors contributed to the discussion and writing of the paper.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

Supplementary information The online version contains supplementary material available at <https://doi.org/10.1038/s41524-021-00533-5>.

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