



## Article

# Perovskite solar cell towards lower toxicity: a theoretical study of physical lead reduction strategy

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## ARTICLE INFO

## Article history:

Received 22 April 2019

Received in revised form 14 May 2019

Accepted 27 May 2019

Available online 6 June 2019

## Keywords:

Perovskite solar cell  
Physical lead reduction  
Low toxicity  
Optical space layer  
Transfer matrix model

## ABSTRACT

The huge performance enhancements of the organometal halide perovskite solar cells (OHPSCs) have appealed enormous attention within recent ten years. Although the rapid growth of the device power conversion efficiency (PCE) has attained over 25%, the contamination of health-hazardous components still holds back its sustainable applications. To reduce the lead usage, many groups have tried chemical lead reduction solutions: substituting the lead by other group 14 metal elements to realize the low-lead OHPSCs. Unfortunately, neither the PCE nor the stability, low-lead OHPSCs all lag far behind the state-of-the-art conventional lead-based OHPSCs. In this work, we present a physical lead reduction (PLR) concept by reducing the perovskite film thickness to restrict the perovskite hazard risk with minor scarification in device performances. Through the simulation of transfer matrix model, we theoretically demonstrated that by introducing the optical space layer, the device PCE could maintain 96% of the original maximum value while attenuating the perovskite film thickness to one-third. This means that the usage of lead can be reduced by ~70% with PLR concept, which could have broad appeal as a new lead reduction strategy towards high performance OHPSCs.

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## 1. Introduction

Since the first attempt to use  $\text{CH}_3\text{NH}_3\text{PbI}_3$  ( $\text{MAPbI}_3$ ) as light harvester in solar cells at 2009, the explored superior photoelectric properties of organometal halide perovskites (OHPs), including high absorption coefficient, long charge diffusion length and large bandgap range, have drawn enormous attention [1–8]. The crystalline compound of OHPs can be described by generic chemical formula  $\text{ABX}_3$ , where A-site cation comprises organic compounds like  $\text{CH}_3\text{NH}_3^+$  ( $\text{MA}^+$ ),  $[(\text{NH}_2)_2\text{CH}]^+$  ( $\text{FA}^+$ ), etc., the B-site stands for lead (Pb), and X is halide ions I, Br, and Cl [7,8]. With the progress in the approach development, morphology optimization and mechanism understanding, the explosive growth of power conversion efficiency (PCE) from 3% to over 25% within ten years, makes the organometal halide perovskite solar cells (OHPSCs) without parallel in the photovoltaic history [9]. In addition, OHPSC offers the low processing costs, making it as a front runner in the key

photovoltaic technology for the sustainable development of human civilization [7,10].

However, the contamination of heavy metal lead is one of the major impediments for the OHPSC commercialization, which raising the concern about the potential public health hazards [11,12]. The risk associated to lead usage is not only presented in the arouse of serious health problems such as the hemoglobin biosynthesis disruption, miscarriage, anaemia and hyperactivity, but also the easy pathway into human body (directly through food, water or air) [13–15]. Hence, to eliminate the large lead usage has become the priority for realizing the commercially available OHPSCs. To this end, the common option is to use the chemical lead reduction (CLR) strategy: replacing the lead by using other group 14 metal elements, such as tin (Sn) or germanium (Ge) [2,15,16]. Early in 2012, Chung et al. [17] have tried to introduce  $\text{CsSnI}_3$  with  $E_g$  of 1.3 eV into solid state dye-sensitized solar cell. Then in 2014, the first OHPSC based on  $\text{MASnI}_3$  was obtained by Noel et al. [11], in which the device PCE was over 6%. Since that, many CLR attempts have been explored to realize low-lead OHPSCs. However, neither the PCE nor the device stability,

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low-lead OHPSC still lags far behind the state-of-art conventional OHPSCs [4,16].

Previous study suggests that the lead is critical to realize the superior photoelectric properties of OHPs [18–20]. The complete substitution of  $\text{Pb}^{2+}$  may not only restrict the stable crystalline structure of OHPs, but also bring new deep defect states [12,19,21,22]. Moreover, the B-site cation needs to be stable in +2 state while the upper group elements such as Sn and Ge are more stable in +4 state [15]. The vibration of the oxidation states can introduce the critical stability issues of the device. Furthermore, the health hazard of using OHPs is not only associated to lead, in which methylamine and iodide also play an important role. Methylamine may affect the modification of cells' DNA and RNA content by inhibiting protein turn-over progress. In addition, the iodine or iodide were indicated to affect the thyroid hormone status in substantially different ways [13,15,23–25]. Hence, the CLR is not a sophisticated option for realizing the low toxic OHPSCs at present.

In this work, we provide a physical lead reduction (PLR) concept (decreasing the perovskite film thickness) to decrease the overall consumption of OHPs in the device while maintaining the high PCE. Through the simulation of the transfer matrix model (TMM), we theoretically demonstrated that by introducing the optical space layer, the optical field distribution inside the perovskite absorber was able to be well optimized. As a result, the device PCE could preserve the 96% of the original maximum value while attenuating the perovskite film thickness to one-third, leading to the ~70% lead reduction in the device.

## 2. Experimental

### 2.1. Materials and solvents

All materials were used as received without further purification, including methylamine iodide (MAI, Dyesol), lead iodide ( $\text{PbI}_2$ , 99.99%, TCI), *N,N*-dimethylformamide (DMF, 99.8%, Across), dimethyl sulfoxide (DMSO, 99.7%, Across), Spiro-OMeTAD (Feiming Chemical Limited), tin oxide colloidal solution ( $\text{SnO}_2$ , 15% in  $\text{H}_2\text{O}$  colloidal dispersion, Alfa Aesar), Zinc oxide nanoparticles ( $\text{ZnO}$  NPs, 2.5 wt% in isopropanol, Sigma-Aldrich).

### 2.2. Transfer matrix model simulation

We use the cubic  $\text{ABX}_3$  perovskite structure, in which the A represents the MA cation ( $\text{CH}_3\text{NH}_3^+$ ), B represents as Pb, and X represents the iodine in this work. Two kinds of device structure are employed for the TMM simulation. Normal structure: indium tin oxide (ITO) (150 nm)/ $\text{SnO}_2$  (150 nm)/ $\text{MAPbI}_3$  (200–600 nm)/Spiro-OMeTAD (abbreviated as Spiro, 100 nm)/Au (100 nm). Inverted structure: ITO (150 nm)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (40 nm)/ $\text{MAPbI}_3$  (200–600 nm)/ $\text{PC}_{61}\text{BM}$  (50 nm)/Ag (100 nm). Optical space layer (OS): OS-1 is  $\text{SnO}_2/\text{ZnO}$  NPs, OS-2 is  $\text{MoO}_3/\text{Spiro}$ , OS-3 is PEDOT:PSS/ $\text{MoO}_3$ , OS-4 is  $\text{ZnO}$  NPs/ $\text{PC}_{61}\text{BM}$ . The optical field distribution and short-circuit current density under AM 1.5 solar illumination were modelled using a Matlab code developed by Burkhard et al. [26] and based on a transfer matrix method described by Petersson et al. [27]. The thickness error is around  $\pm 10$  nm for the perovskite film, and  $\pm 2$  nm for the optical space layer.

### 2.3. Characterization

The UV–vis absorption spectra of  $\text{MAPbI}_3$  film were measured by a spectrophotometer (UH4150, Hitachi). The real part of the refractive index ( $n$ ) was determined from a transformation of the

Kramers-Kronig relation from the extinction coefficient ( $k$ ) and base-lined with  $n$  ( $\lambda > 800$  nm) extracted from the spectroscopic ellipsometry data collected on an ellipsometer (Nanoview SE MF-1000).

## 3. Results and discussion

According to the literatures, high efficient OHPSCs are generally based on the thick perovskite absorber with a film thickness about 400–600 nm. The advantages of using such thick films can be concluded as: (1) profiting from the long carrier diffusion length over the orders of micrometers, the perovskite absorber can be fabricated thick enough to absorb the light completely [28,29]. (2) Thick film can relieve the pin-hole issues which are highly problematic in the thin film solar cell [19,30]. (3) The effect of the thickness deviation error to the device performance is inverse proportion to the film thickness [31,32]. (4) Thick film is more favor for the scalable manufacture methods such as roll-to-roll, spray coating and blade casting, etc. [6,32,33]. However, the thicker perovskite absorber means the larger toxic component usage, which raises the risk of health hazards. Although many CLRs have been developed to alleviate the hazard worries, these solutions are still far from mature, which mainly restricted by the low PCE and weak device stability. Hence, we provide a PLR strategy for the future commercial OHPSC in this work. Compared to CLR, PLR curtails the original perovskite materials input by decreasing the perovskite film thickness, as described in Fig. 1. Through optimizing the optical field distribution, the thinner perovskite film can preserve the high device performance with less lead usage, which paves the way for the future commercialized OHPSCs.

To estimate the performance of thin-film OHPSCs, we need to investigate the influence of thickness on the device parameters at first. According to the definition of solar cell performance,

$$\text{PCE} = \frac{J_{\text{sc}} \cdot V_{\text{oc}}}{P_{\text{in}}} \text{FF}, \quad (1)$$

where  $J_{\text{sc}}$  is the short-circuit current density,  $V_{\text{oc}}$  is the open-circuit voltage,  $P_{\text{in}}$  is the incident power, and FF is the fill factor. As well known, the perovskite absorber can generate the charges by directly absorbing the insight light. The  $J_{\text{sc}}$  is mainly determined by the perovskite component combination and the charge generation rate of the absorber. In this work, we choose the most widely explored  $\text{MAPbI}_3$  ( $\text{MA}^+ = \text{CH}_3\text{NH}_3^+$ ) as the perovskite absorber material. Among the photovoltaic parameters, internal quantum efficiency (IQE) is the ratio of the extracted charge carriers to the captured sunlight in the absorber. For the OHPSC, many researches have demonstrated the extra high IQE. To simplify the simulation progress, we assume the IQE = 100%, which means every absorbed photon can be transferred to generate exciton. Hence, the  $J_{\text{sc}}$  varying as a function of device geometry and perovskite absorber thickness becomes possible. As depicted in Fig. 2a, the absorption of  $\text{MAPbI}_3$  film can be distinguished as two regimes of behavior: Beer-Lambert regime ( $\lambda < 650$  nm) and cavity regime ( $\lambda > 650$  nm). Perovskite shows a strong light absorbance for the Beer-Lambert regime light. Hence, thin perovskite film could realize the completely light absorption. In contrast, the perovskite exhibit relatively low absorption efficiency for the cavity regime light.

To understand the cavity electro-optics of OHPSCs, the optical constants of all layers need to be accurately measured. The refractive index  $n$  determines the wavelength of light in a material and extinction coefficient  $k$  is related to the absorption in the medium [26,34]. Although there are several ( $n$ ,  $k$ ) data that can be found online, the optical constants of materials may affected by the fabrication conditions. To make sure the accuracy of our simulation, we apply the spectroscopic ellipsometry to characterize the optical

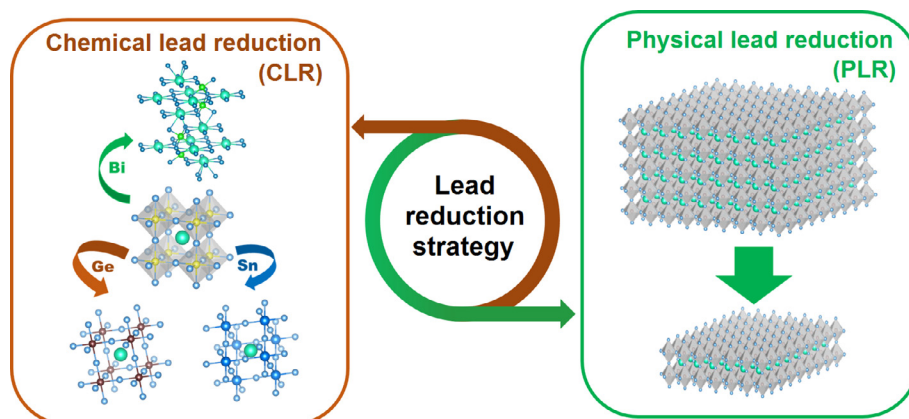


Fig. 1. (Color online) Lead reduction concept for low toxic OHPSCs.

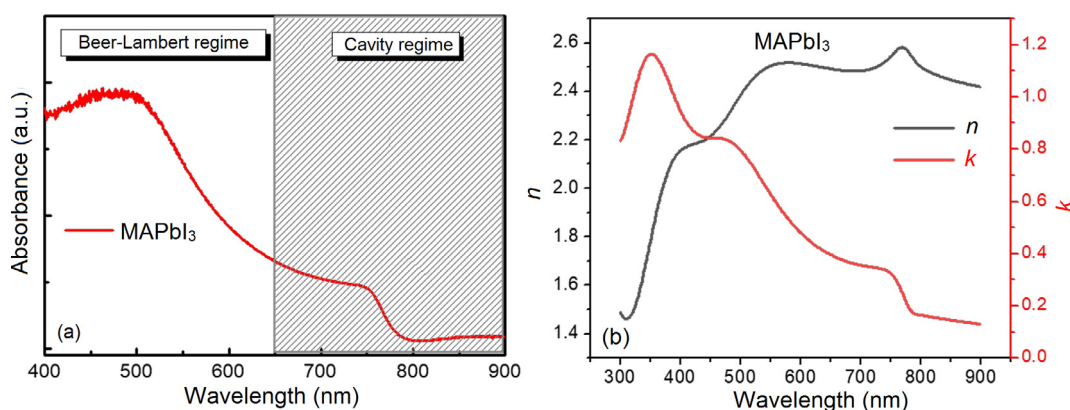


Fig. 2. (Color online) Absorption spectra of 600 nm MAPbI<sub>3</sub> film (a) and optical constants of MAPbI<sub>3</sub> (b).

constants for all layers used in this work. The optical constants of MAPbI<sub>3</sub> is presented in Fig. 2b, while other material details can be found in the Fig. S1 (online).

The transfer matrix method can be used to model the absorption of absorber layer, accounting for the optical interference effect as well as parasitic absorption [26,34]. This method has been well utilized in the prediction of the organic solar cell performance, and also dedicated to the research of OHPSCs recently [35–38]. To demonstrate the universality of this method, the most widely used device structures were chosen for the TMM simulation, which is normal structure (ITO/SnO<sub>2</sub>/MAPbI<sub>3</sub>/Spiro/Au) and inverted structure (ITO/PEDOT:PSS/MAPbI<sub>3</sub>/PC<sub>61</sub>BM/Ag). Fig. 3a shows the optical field distribution in the OHPSCs for the four wavelengths of

500–800 nm. Be strongly absorbed by MAPbI<sub>3</sub>, the incident light with  $\lambda < 650$  nm follows the Beer-Lambert law that cannot reach the back electrode. In this case, the absorption is saturated without the appearance of optical interference. In contrast, the light with  $\lambda > 650$  nm exhibited the low finesse cavity interference [34]. According to TMM, we estimated the maximum photocurrent to be near 24.26 mA cm<sup>-2</sup>, assuming the IQE of 100% (Fig. 3b). It suggests that the contribution of photocurrent mainly originates from the first few hundred nanometers. The reason for the fabrication of thick film over 400 nm is to confirm the saturated absorption of incident light. To explore the minimum absorber thickness, we simulate the maximum  $J_{sc}$  as a function of the perovskite absorber thickness (Fig. 3c). It shows that the turning point of this curve is

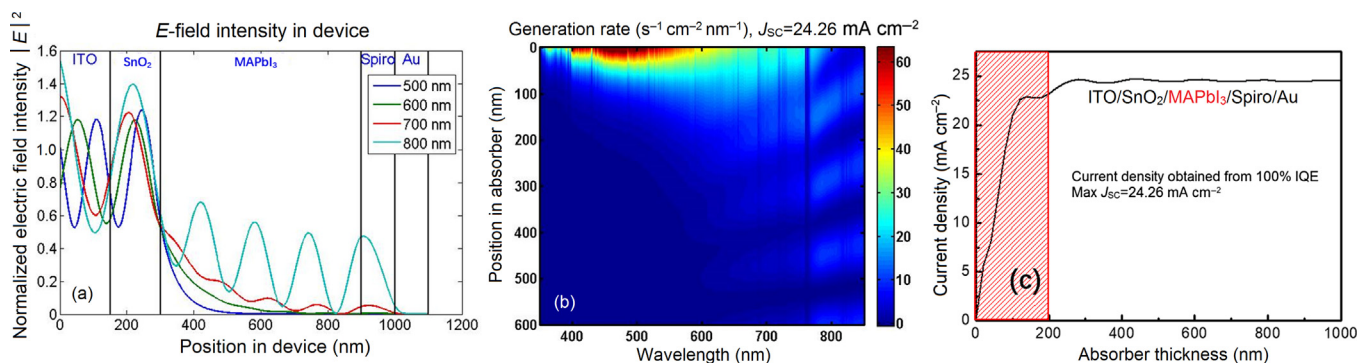


Fig. 3. (Color online) (a) Optical field distribution in MAPbI<sub>3</sub> based OHPSC for four wavelengths of 500–800 nm. (b) Exciton generation rate distribution among the MAPbI<sub>3</sub> layer. (c) Calculated perovskite absorber thickness vs. short circuit current density.

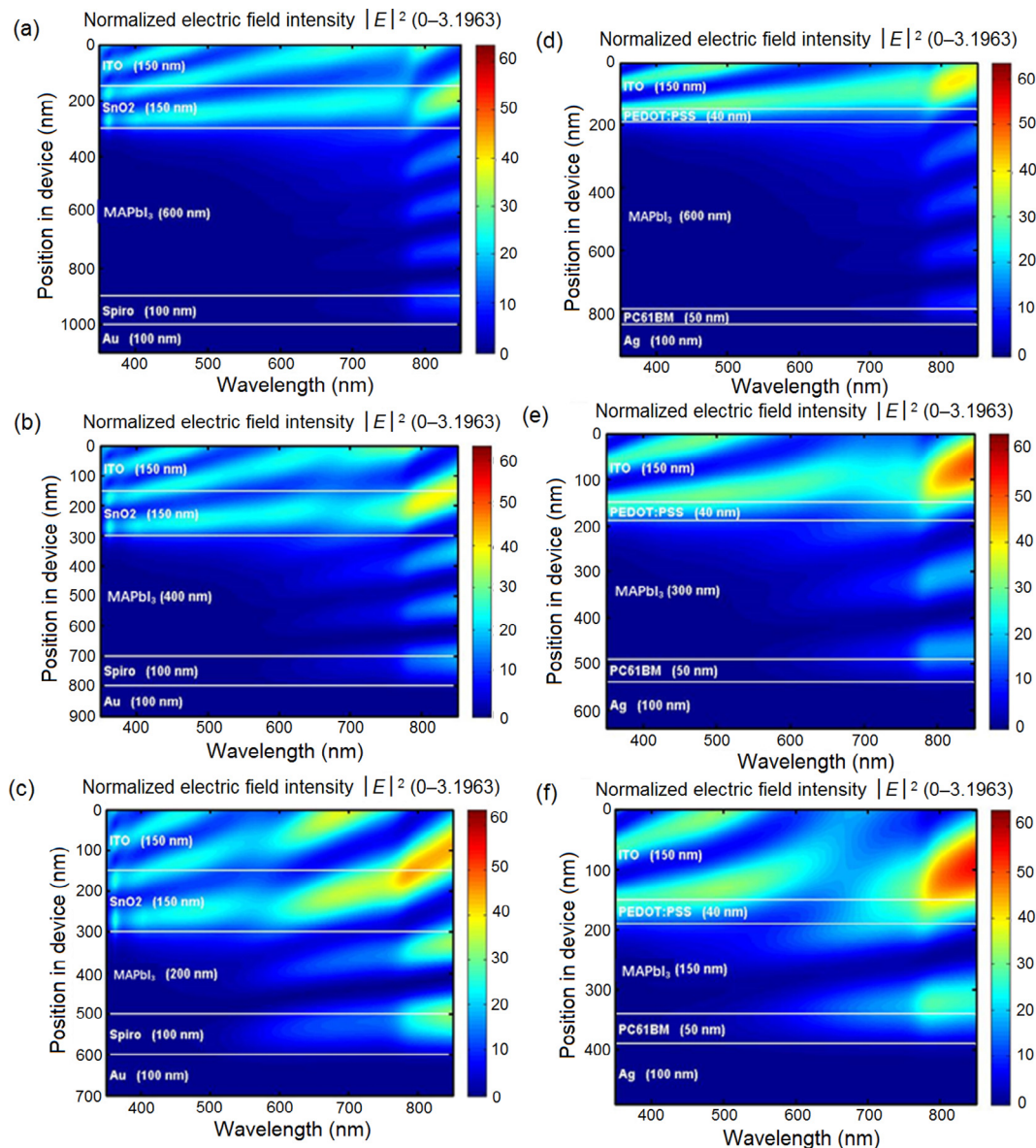


found in 200 nm, in which the  $J_{SC}$  have reached the 85% of maximum value. This phenomenon is also shown in the inverted structured OHPSC, where the absorber thickness can be further decreased to 150 nm (Fig. S2 online). After the turning point, the  $J_{SC}$  exhibits independence of the film thickness. This indicates the perovskite film can be fabricated as thin as 200 nm while maintaining the high photovoltaic performance.

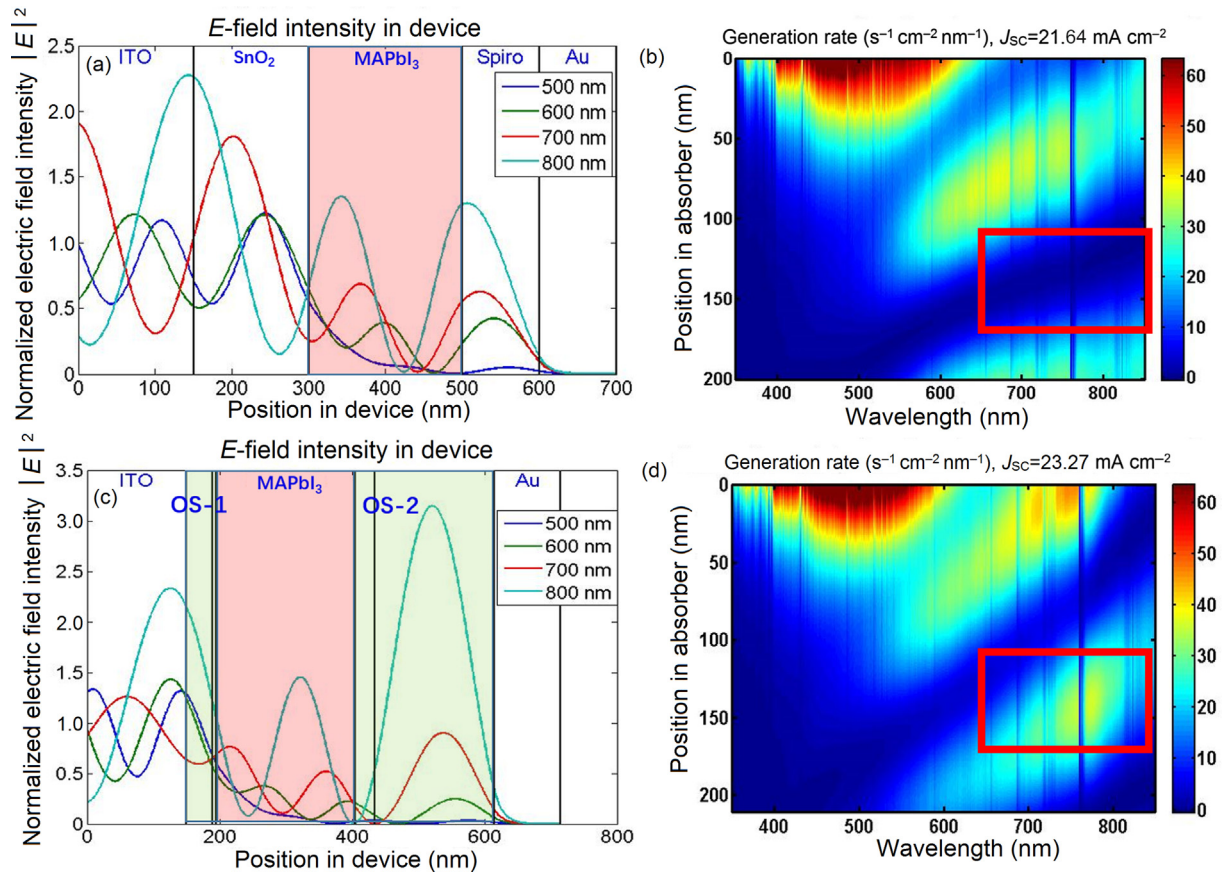
To further investigate the effect of film thickness to the optical field distribution, we simulate the OHPSC with varied structure (Figs. 4 and S3 (online)). In the normal device, the optical interference exhibited more significantly with the decrease of the perovskite film thickness. When the film is thick enough (>400 nm), only the light of  $\lambda > 650$  nm shows the optical interference effects in the perovskite layer. However, the strong optical peaks and valleys were emerged when the perovskite thickness decreases to 200 nm. The excitation distribution in fact is discontinuous at the interface since the optical constant changes at the interface. It is seen that  $|E|^2$  is strongly influenced by interference effects, which gives rise to a varying value in the device [27]. Due to the different

charge transport materials used in normal and inverted structure, the optical field distribution shows the differential peaks and valleys within the perovskite absorber. For the light located in Beer-Lambert regime, 200 nm film thickness is thick enough for the saturated light absorption. However, the light in the cavity regime still suffers from the optical interference effects, in which the interference valley restricts the exciton generation rate.

In order to optimize the optical distribution inside the absorber layer, we need to modify the contact between perovskite absorber and charge transport layer. Based on the previous results, we chose molybdenum trioxide ( $\text{MoO}_3$ ) and zinc oxide nanoparticles ( $\text{ZnO}$  NPs) as the optical spacer [39–41]. To simplify, we combine optical spacer and charge transfer layer as optical space layer. Figs. 5 and S3 (online) exhibit the optical distribution inside the OHPSCs with and without optical space layer. As shown in Fig. 5a and b, normal structure OHPSC only shows one interference peak ridge for the cavity regime light within the perovskite absorber, giving rise to the  $J_{SC}$  of 21.64  $\text{mA}/\text{cm}^2$ . In comparison, through the calculation of TMM, we obtained the two interference ridges of cavity regime



**Fig. 4.** (Color online) Normalized electric field intensity distribution in the OHPSC with normal structure (a–c) and inverted structure (d–f).  $\text{MAPbI}_3$  thickness varies from 600 to 200 nm.



**Fig. 5.** (Color online) Optical field distribution of OHPSCs. (a) and (c) The optical field distribution in MAPbI<sub>3</sub>-based normal OHPSC for four wavelengths of 500–800 nm. (b) and (d) The corresponding exciton generation rates distribution among the MAPbI<sub>3</sub> layer. The box inside Fig. 5d shows the second interference ridge.

by optimizing the thickness of OS, resulting in the enhanced  $J_{SC}$  of 23.27 mA/cm<sup>2</sup> (Fig. 5c and d). Similarly, we accessed the  $J_{SC}$  improvement from 20.82 to 22.19 mA/cm<sup>2</sup> by adjusting the OS thickness in the inverted OHPSCs.

To evaluate the device performance, we combine the Shockley-Queisser theory and detailed balance principle for the estimation of  $V_{OC}$  and  $FF$  [42]. Regardless the nonradiative recombination (defect-assisted recombination and Auger recombination, etc.), the  $V_{OC}$  can be calculated by measuring the film absorption (details can be found in Supplementary data online) [17–19,21,42]. In addition, the  $V_{OC}$  can deduce to the  $FF$  through empirically forum

$$FF = \frac{v_{OC} - \ln(v_{OC} + 0.72)}{v_{OC} + 1}, \quad (2)$$

$$v_{OC} = \frac{q}{nkT} V_{OC}, \quad (3)$$

where the  $v_{OC}$  is defined as “normalized  $V_{OC}$ ”. Hence, we can obtain the PCE of the thin film OHPSC through Eq. (1), and the estimated photovoltaic parameters are listed in the Table 1. The theoretical results show that by introducing the OS, the PCE of device can still maintain the 96% of the maximum value while reducing the perovskite absorber thickness to 200 nm. Compared with that, the absorber thickness could be even decreased to 150 nm for the inverted OHPSCs, which also preserved over 96% of the original PCE.

In addition to the high PCE, the fabrication of thin film OHPSC would bring a significant commercial benefit. Although the cost of OHPSC is relatively low when compared to other 3rd generation photovoltaic technologies, the utilization of toxicity and health-hazardous components hold back the further commercial application of OHPSCs [7,13]. Through the theoretical study in this work, we have demonstrated the perovskite film could be fabricated as thin as 150 nm while maintain the 96% PCE of OHPSCs based on 600 nm thick perovskite absorber. Assuming all electric power

**Table 1**  
Simulated photovoltaic parameters of OHPSC.

| OHPSC structure |                                                          | Absorber thickness (nm) | $J_{SC}$ (mA cm <sup>-2</sup> ) | $V_{OC}$ (V) | $FF^c$ (%) | PCE (%) |
|-----------------|----------------------------------------------------------|-------------------------|---------------------------------|--------------|------------|---------|
| Normal          | ITO/SnO <sub>2</sub> /MAPbI <sub>3</sub> /Spiro/Au       | 600                     | 24.26                           | 1.36         | 90.71      | 29.93   |
|                 | ITO/SnO <sub>2</sub> /MAPbI <sub>3</sub> /Spiro/Au       | 200                     | 21.63                           | 1.34         | 90.60      | 26.25   |
|                 | ITO/OS-1/MAPbI <sub>3</sub> /OS-2/Au <sup>a</sup>        | 200                     | 23.27                           | 1.34         | 90.60      | 28.25   |
| Inverted        | ITO/PEDOT:PSS/MAPbI <sub>3</sub> /PC <sub>61</sub> BM/Ag | 600                     | 22.72                           | 1.36         | 90.71      | 28.03   |
|                 | ITO/PEDOT:PSS/MAPbI <sub>3</sub> /PC <sub>61</sub> BM/Ag | 150                     | 20.81                           | 1.33         | 90.55      | 25.06   |
|                 | ITO/OS-3/MAPbI <sub>3</sub> /OS-4/Ag <sup>b</sup>        | 150                     | 22.19                           | 1.33         | 90.55      | 26.72   |

<sup>a</sup> OS-1: SnO<sub>2</sub> (40 nm)/ZnO NPs (10 nm); OS-2: MoO<sub>3</sub> (3 nm)/Spiro (180 nm).

<sup>b</sup> OS-3: PEDOT:PSS (40 nm)/MoO<sub>3</sub> (10 nm); OS-4: ZnO NPs (20 nm)/PC<sub>61</sub>BM (50 nm).

<sup>c</sup>  $FF$  was calculated under the ideality factor  $n = 1$ .

generation OHPSCs are based on MAPbI<sub>3</sub> absorber, to the maximum extent, the utilization of thin film OHPSCs can avoid the usage of 40 tons Pb, as well as 73.49 and 6.18 tons for iodine and MA, respectively. The less raw materials input can not only decrease the materials cost, but also save the energy wastes in the OHPSC recycling and environmental governances [10,14]. However, this work is only a theoretical prediction of the PLR without showing any experimental results of the ultrathin OHPSCs. Before the optimization of the perovskite precursor, interfacial contact, and optical distribution, the PCE of ultrathin OHPSC is still far from 20%. The obtain of effective optical spacer will be critical for not only the formation of perfect perovskite absorber but also the realization of PLR.

#### 4. Conclusions

In summary, we proposed a PLR strategy to alleviate the health hazard worries of OHPSC by significantly reducing the lead usage. Through the TMM simulation, we theoretically demonstrated that by introducing the optical space layer between electrode and perovskite layer, the optical field distribution inside the perovskite absorber is able to be well optimized. As a result, the device PCE could preserve the 96% of the original maximum value while attenuating the perovskite thickness to one-third, leading to ~70% reduction of lead usage. Without reconfiguration the combination of perovskite components, our unique approach could have board appeal as a new lead reduction strategy towards high performance OHPSCs and commercial available perovskite electronics.

#### Conflict of interest

The authors declare that they have no conflict of interest.

#### Acknowledgments

This work was supported by the National Basic Research Program of China (2015CB932203), the National Natural Science Foundation of China (91733301, 61722501, 61377025, 91433203, and 61604121), and Postdoctoral Innovative Talents Support Project (8206200013).

#### Author contributions

R. Zhu and Y. Zheng conceived the idea and designed the experiment. Y. Zheng and R. Su conducted the TMM simulation. Z. Xu carried out the absorption measurement. D. Luo optimized the MATLAB simulation program. H. Dong and B. Jiao made contribution to the optical constants measurement. All the authors analyzed the data and contributed to the discussion. Y. Zheng wrote the manuscript with input from all co-authors. R. Zhu and Z. Wu revised the paper. R. Zhu and Q. Gong supervised the project.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scib.2019.06.006>.

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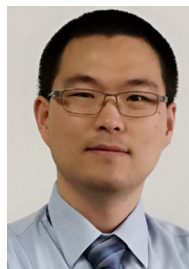
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