Simulation study towards high performance transparent-conductive-oxide free perovskite solar cells using metal microcavity and optical coupling layer

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Abstract: The microcavity perovskite solar cells (PSCs) are designed by sandwiching the perovskite layer between the ultra-thin Ag and opaque Ag electrodes. Compared to transparent-conductive-oxide (TCO) based PSCs, the microcavity PSCs with the bare Ag electrode shows the poor optical performance due to the transmittance limit of Ag film. By introducing an optical coupling layer, the remarkably improved transmittance of Ag electrode and enhanced light absorption in the perovskite layer are obtained. Furthermore, the better light absorption is available by adopting an optical spacer, and the resulted microcavity PSCs achieve the comparable or even higher JSC than TCO-based PSCs. This provides a guideline to design and fabricate efficient TCO-free PSCs.

Index Terms: Microcavity, ultrathin Ag film electrode, optical coupling layer, perovskite solar cells.

1. Introduction

Organic–inorganic lead halide perovskite solar cells (PSCs) have attracted much attention due to their advantages of low fabrication cost, high light absorption coefficient, high charge carrier mobility, long charge diffusion length, tunable band-gap, high power conversion efficiency (PCE), and stably improved operating lifetime[1–4]. Nowadays, their highest PCE has reached 22.1% [5], and the PCE for large area PSCs has also exceeded 18.21% (1.022 cm²) and 12% (36.1 cm²) [6]. And their operating lifetime has also enabled testing over a timescale from several hours to thousands of hours[7]. These great progresses should be attributed to the efforts of worldwide researchers from the aspects of device structure, composition engineering, interface engineering, electrode engineering, and various fabrication methods or treatments [8–13]. And to realize the large-scale commercial application, not only the better performance but also the lower cost are urgently desired.

Indium-tin-oxide (ITO) and fluorine-tin-oxide (FTO) are the most commonly used transparent oxide electrodes. However, due to the limited reserve and toxicity of indium, high sheet resistance, high temperature sputter process, poor mechanical ductility, and increasing price, more research efforts have focused on the ITO (or FTO) free transparent conductors. Now, the reported alternatives mainly include graphene[14], carbon nanotubes[15], Ag nanowire[16], patterned metal grids[17], and metal films[18]. Among them, the metal thin films (for example Ag) are more suitable for the mass production due to the simple thermal evaporation process, high conductivity, relatively low optical absorption, and intrinsic flexibility. In our previous works, the optimal MoO3(2 nm)/Ag(9 nm) film anode has been successfully used to fabricate efficient organic solar cells and flexible devices[19,20]. Also the bifacial semitransparent PSCs employing PEIE/Ag(10 nm)/MoO3 triple-layer cathode obtained good bifacial photovoltaic performance [12].

On the other hand, an optical microcavity can be formed by sandwiching the photoactive material between two reflective metal electrodes of ultra-thin and opaque metal films, which has been proved available to adjust the optical electric field distributions and enhance the light absorption in the photoactive materials. This microcavity-enhanced structure has been widely used in polymer solar cells, photo-detectors, and light-emitting diodes (LEDs) [21–24]. Our previous calculations have systematically shown the optical electric field adjustments and light absorption enhancement inside the thieno[3,4-b]thiophene/benzodithiophene: [6,6]-phenylC71-butyric acid methyl ester (PTB7:PC71BM) based polymer solar cells using ultrathin Ag film electrode, and the corresponding devices achieve comparable photocurrent and also exhibit a light absorption enhancement at relatively long wavelength [25]. When it comes to perovskite solar cells, many researches focus on color-tunable PSCs based on Ag/ITO/Ag[26] or Ag/dielectric medium/Ag microcavity structures[27], which greatly promotes the possible applications of photovoltaic windows and buildings. While the light absorption enhancement for microcavity based ITO (or FTO) free PSCs are rarely reported.

In this work, the Ag(opaque)/perovskite/Ag(ultra thin) sandwiched optical microcavity is systematically investigated to enhance the light absorption in ITO (or FTO) free based PSCs, and seek the feasibility of efficient light harvesting PSCs structures. According to the optical calculations by transfer matrix method, the microcavity PSCs with ultrathin Ag (8 nm) electrode shows relatively lower JSC and light absorption compared to ITO (or FTO) based PSCs with conventional and inverted structures, which is mainly due to the light transmittance limit of Ag film. By introducing a tellurium oxide (TeO2) optical coupling layer with high dielectric constant, the
TeO₂(36nm)/Ag electrode obtains obviously improved transmittance. Thus the corresponding bottom-illuminated PSCs shows remarkably improved short circuit current density \( J_{SC} \) and light absorption ability, and the top-illuminated PSCs exhibit better optical performance and higher \( J_{SC} \). Also the conventional PSCs performs better than that of inverted PSCs. Fortunately, by inserting an optical spacer of bathocuproine (BCP) or poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), the redistribution of optical electric field results in further improved light absorption for inverted PSCs with various thickness perovskite layer. The results indicate that both conventional and inverted PSCs with an optical microcavity could obtain comparable or even better optical performance than PSCs with transparent oxide electrode, which provides a guideline to design and fabricate efficient TCO-free PSCs.

2. Method

To understand the structure dependent optical performance of PSCs and the optical mechanism of microcavity resonances, the widely used transfer matrix method \([28, 29]\) is adopted to calculate the light absorption spectrum, the maximum possible \( J_{SC} \), the optical electric field distribution, and the exciton generation rate in microcavity PSCs. In the optical simulations, the internal quantum efficiency is assumed as 100%, namely all the absorbed photons can be transformed into free charges; the normally incident AM 1.5G solar spectrum is chosen as light source; the optical constants obtained from references \([30,31]\) layer and layer thicknesses are used as input parameters of the optical model. The calculation details and optical interference theory could be found in our previous works and other reports \([32–34]\).

In this work, the optical performance of planar PSCs with conventional structure, inverted structure, bottom and top illuminated microcavity structures is systematically investigated. As shown in Fig. 1, the typical CH₃NH₃PbI₃ is chosen as photoactive layer, the PEDOT:PSS and spiro-OMeTAD act as hole transport layer (HTL), the titanium dioxide (TiO₂) and phenyl-C₆₁-butyl acid methyl ester (PCBM) play the role of electron transport layer (ETL), the ITO (or FTO) and opaque Ag serve as the electrodes. In particular, the opaque Ag and ultra thin Ag film form the optical microcavity, and the high dielectric TeO₂ is selected as the optical coupling layer to adjust the transmittance of ultrathin Ag electrode. The conventional FTO-based PSC and inverted ITO-based PSC are reference devices, and the microcavity structured PSCs can be illuminated from the top and bottom directions.

For convenience, the reference devices of Glass/FTO(350nm)/TiO₂(50nm)/CH₃NH₃PbI₃(300nm)/spiro-OMeTAD(150nm)/Ag(100nm) and Glass/ITO(180nm)/PEDOT:PSS(10nm)/CH₃NH₃PbI₃(300nm)/PCBM(50nm)/Ag(100nm) are marked as Device R1 and Device R2, which represent the conventional and inverted planar PSCs, respectively. The thickness of various layers is selected according to typical experiment values. The corresponding microcavity PSCs of Device M1 (or Device M2) show the geometry of Glass/TeO₂(36nm)/ultrathin Ag(8nm)/TiO₂ (or PEDOT:PSS)/CH₃NH₃PbI₃/spiro-OMeTAD (or PCBM)/opaque Ag(100nm). And the top-illuminated PSCs of Device TM1 and Device TM2 have the same structures as Device M1 and M2 expect the opposite position of glass substrate and light illumination directions, as shown in Fig. 1. The marks for devices with various structures are summarized in Table s1 (seeing supplementary materials). It must be pointed out that the calculations mainly focus on the optimizing design of Ag electrode and device structure, the thickness of most stack layers have been fixed according to the typical experiment values in our laboratory. Thus the following discussion is design-dependent in this work, and the optimizing parameters in different experiment environments maynot be the same, while the method presented here could provide a guideline to the specific design of PSCs.

3. Results and discussion

3.1 Microcavity PSCs with conventional structure

The calculated maximum possible short circuit current density \( J_{SC} \) as a function of CH₃NH₃PbI₃ thickness, and the wavelength dependent light absorption for Device M1, Device TM1 and Device R1 are shown in Fig 2(a) and (b). It is clear from Fig 2(a) that, all
the maximum possible J_{SC} values increase with the CH_3NH_3PbI_3 thickness and shows the obvious oscillation behavior. The increased J_{SC} comes from better light absorption in thicker perovskite layer and the oscillation behavior should be attributed to the optical interference between incident light and reflective light from back Ag electrode[21,25]. It should be noted that the J_{SC} of microcavity Device M1 and TM1 are seriously lower than that of reference Device R1, which is due to the higher optical transmittance of FTO than ultrathin Ag film (8nm) electrode. Here, to modulate the Ag film transmittance, the high dielectric TeO_2 optical coupling layer is employed, then the resulted Devices M1 and TM1 possess the light incident electrodes of Glass/TeO_2(36nm)/Ag(8nm) or TeO_2(36nm)/Ag(8nm), and the thicknesses optimization will be discussed later. Compared to the original Device M1 and TM1, shown in Fig.2(a), the TeO_2 modified PSCs obtain a remarkable improvement in J_{SC}, which is very close to or even higher than that of reference Device R1. This can be understood that, the TeO_2 coupling layer, behaving like an anti-reflective coating, minimizes the reflected loss of the incident light and enhances the transmittance of Ag electrode. Thus the increased incident photons in a microcavity prominently facilitates the optical interference and resonant effect, an than the improved light absorption in the perovskite layer is responsible for the enhanced J_{SC} of PSCs. Additionally, the increased optical transmittance of TeO_2/Ag electrode may be explained by the fact that a higher dielectric layer (ε_{TeO2} = 25) can suppress a large optical dissipation related to the emission of non-radiative surface plasmons at the interface of dielectric layer and Ag film (ε = 9.7). This mechanism has been theoretically and experimentally confirmed by our previous works[12,25] and other reports[21, 35-37], and the detail description could be found in reference [38].

![Graph](image)

**Fig. 2 (a) J_{SC} as a function of CH_3NH_3PbI_3 thickness and (b) wavelength dependent light absorption fraction for Device R1, Device M1 and TM1 with and without TeO_2 optical coupling layer.**

<table>
<thead>
<tr>
<th>Devices</th>
<th>J_{SC} (mA/cm^2) at CH_3NH_3PbI_3 thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Device R1</td>
<td>22.17 (300 nm)</td>
</tr>
<tr>
<td>Device M1</td>
<td>18.50 (Ag(8nm))</td>
</tr>
<tr>
<td>Device TM1</td>
<td>18.12 (Ag(8nm))</td>
</tr>
<tr>
<td>Devic R2</td>
<td>21.73 (ITO)</td>
</tr>
<tr>
<td>Device M2</td>
<td>15.34 (Ag(8nm))</td>
</tr>
<tr>
<td>Device TM2</td>
<td>20.93 (TeO_2/Ag)</td>
</tr>
<tr>
<td></td>
<td>16.33 (Ag(8nm))</td>
</tr>
<tr>
<td></td>
<td>21.41 (TeO_2/Ag)</td>
</tr>
</tbody>
</table>

On the other hand, as the typical thickness of CH_3NH_3PbI_3 processed from one-step or two-step methods are about 250-350 nm in our laboratory, the 300 nm thick CH_3NH_3PbI_3 is chosen to further study the wavelength dependent light absorption for microcavity and reference PSCs. The calculation results are shown in Fig.2(b) as well the corresponding J_{SC} in Table 1. From Fig. 2(b), the microcavity based Device M1 shows relatively poor light absorption in the range from 550 nm to 800 nm compared to Device R1, which agrees with the lower J_{SC} of 18.50 mA/cm^2 for Device M1. When the TeO_2(36nm)/Ag(8nm) electrode is introduced, the light absorption in Device...
M1 enhances observably in the whole range from 350 to 800 nm and the improved J_{SC} of 22.64 mA/cm^2 is obtained, which is comparable to or even better than that of Device R1. Simultaneously, for the top illuminated Device TM1, the absorption loss below 400 nm comes from the parasitic absorption in spiro-OMeTAD material, and the insertion of TeO\textsubscript{2} coupling layer results in an obvious absorption improvement from 650 nm to 780 nm. Meanwhile the optimized J_{SC} is as high as 22.81 mA/cm\textsuperscript{2}. In short, for conventional PSCs, the optimized microcavity PSCs with ultrathin Ag film electrode shows comparable optical performance to FTO based PSCs, which illustrates the potential applications of microcavity structure for efficient FTO-free PSCs.

At the same time, the transparent electrode with high transmittance and conductivity is required to obtain efficient PSCs. In this work, the optimizing thickness of 8 nm Ag film and 36 nm TeO\textsubscript{2} coupling layer is acquired from the calculation results shown in Fig. 3. It is clear that the calculated transmittance of Ag film decreases with its thickness from 11 to 8 nm, and the TeO\textsubscript{2} optical couple layer could remarkably enhance the Ag transmittance especially in the long wavelength range from 500 to 800 nm (higher AM1.5G photon flux), which is responsible to the prominently improved J_{SC}. This is due to the higher transmittance or lower parasitic absorption in thinner Ag film and improved light absorption in CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} material. It is noteworthy that the conductivity of Ag film is determined by its percolation threshold thickness. In our laboratory, the percolation threshold of thermally evaporated Ag film can been decreased from 11 nm to 9 nm by the MoO\textsubscript{3} surface energy modifying layer, and the thinner 8 nm has been experimentally reported\[39\]. Therefore, due to the instability of thinner Ag, here the 8 nm thick Ag film is chosen as another metal mirror to form optical microcavity with opaque Ag electrode. The introducing of TeO\textsubscript{2}/Ag transparent electrode leads to the prominently improved J_{SC} and the optimized TeO\textsubscript{2} thickness is 36nm.

![Image](image_url)

Fig. 3 (a) Calculated optical transmittance for Ag film with various thickness and TeO\textsubscript{2}(36 nm)/Ag(mm) electrode. The glass substrate is not included in calculations. (b) Calculated J_{SC} for PSCs with Ag (8nm) electrode and TeO\textsubscript{2}(36 nm)/Ag(mm) electrode. Inset: effect of TeO\textsubscript{2} thickness on calculated J_{SC}.

### 3.2 Microcavity PSCs with inverted structure

The calculated J_{SC} as a function of CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} thickness, and wavelength dependent light absorption for inverted PSCs, Device M2 and R2, are shown in Fig.4(a) and (b); as well the corresponding J_{SC} values at typical CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} thickness about 300 nm and 450 nm are displayed in Table 1. Their J_{SC} shows the similar oscillation behavior to conventional Device M1 and R1, and the transmittance limit of 8 nm Ag film is responsible for the inferior performance of Device M2 than Device R2. Then the J_{SC} of Device M2 improves remarkably when the TeO\textsubscript{2} transmittance enhancement layer is introduced. Furthermore, an optical spacer of BCP (50nm) is inserted between PCBM and Ag to modulate the optical electric field distribution in microcavity and the J_{SC} of Device M2 is further enhanced to 21.42 mA/cm\textsuperscript{2}. Fig. 4(c) shows the optical electric filed distributions at 500, 650, and 750 nm in CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} absorber for Device M1. By inserting the BCP layer, it is clear that the electric field intensity at 500 nm or 650 nm is nearly unchanged or slightly reduced, however, both the electric field intensity maxima and the area below the curve are enhanced at 750 nm, which leads to more intensive photon energy in CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} and increased light absorption possibility. This is in line with the light absorption fraction at 500, 650, 750 nm in Fig. 4(b) and relatively higher excitation generation rate for Device M2 with BCP spacer shown in insert of Fig.4(c). Simultaneously, from the electrical aspect, the BCP possesses deep HOMO energy level of 7.0 eV and low LUMO energy level of 3.5 eV, which could efficiently block the hole and facilitate the electron transport at PCBM/Ag interface [9]. The optimization of BCP and PCBM thicknesses can be found in Fig. s1(a)(seeing supplementary materials), and their optimized thicknesses are 50 nm. Thus the Device M2 with optimizing PCBM/BCP/Ag transparent electrode shows comparable optical performance to Device R2, demonstrating the feasibility of efficient microcavity PSCs with inverted structure.

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When it comes to top illuminated inverted PSCs, the calculated $J_{SC}$ and light absorption fraction for Device TM2, M2, and R2 are shown in Fig. 5(a) and (b). The similar oscillation tendency can be observed from the $J_{SC}$ of Device TM2, and the relatively poor $J_{SC}$ performance for Device TM2 has been distinctly improved by introducing the TeO$_2$ (36 nm) coupling layer. However, it should be noted that, both the original or TeO$_2$ modified Device TM2 have obtained higher $J_{SC}$ than that of Device M2 at most CH$_3$NH$_3$PbI$_3$ thicknesses, which could be attributed to the removing of absorption and reflection loss in glass under the condition of top illumination. Further we investigate the thickness effect of PEDOT:PSS from 10 to 150 nm (see Fig. s1b in supplementary materials), and the senior $J_{SC}$ has been achieved for PSCs with 250-310nm thick CH$_3$NH$_3$PbI$_3$ layer when the 90nm PEDOT:PSS is used. Simultaneously, with the CH$_3$NH$_3$PbI$_3$ thickness fixed at 300nm, as shown in Fig. 5(b), Device TM2 shows better absorption in the wavelength range from 450 to 700 nm than that of Device M2; while the TeO$_2$ modified Device TM2 achieves dramatically enhanced light absorption at nearly all the wavelength; and furthermore Device TM2 with 90nm PEDOT:PSS displays obvious absorption enhancement at the long wavelength range. This is in line with the nearly unchanged or calculated $J_{SC}$ values in Table 1. Here, it is thought that the further improved performance for Device
TM2 results from the redistribution of optical electric field in CH$_3$NH$_3$PbI$_3$ layer caused by thicker (90 nm) PEDOT:PSS optical spacer. It can be seen in Fig. 5(c) that, both the electric field intensity maxima and the area below the curve are enhanced at 750 nm, which facilitates the light absorption in CH$_3$NH$_3$PbI$_3$ layer. This agrees well with the better light absorption fraction at 750 nm in Fig. 5(b). Also the slightly improved exciton generation rate in the inset of Fig. 5(c) and improved $J_{SC}$ in Table 1 confirm the above discussions. What is more, when the 450 nm CH$_3$NH$_3$PbI$_3$ layer is used, the microcavity structure stills work well and the PSCs also obtains comparable $J_{SC}$ values to reference PSCs. In addition, when the CH$_3$NH$_3$PbI$_3$ thickness is about 200 nm, a $J_{SC}$ interference maximum appears for Device TM2 and the TeO$_2$ modified PSC exhibit higher $J_{SC}$ than Device R2 at the thickness of 170-250 nm. Although increasing the perovskite thickness for better light absorption is one important route to achieve higher conversion efficiency, this work also provides a feasibility to obtain comparable $J_{SC}$ with relatively thin perovskite photoactive layer. Therefore, the top illuminated microcavity PSCs with optimizing stack layers shows comparable or even better optical performance to ITO based PSCs. It should be noted that the maximum possible $J_{SC}$ is calculated under the assumption of 100% external quantum efficiency, the effect of doping, density of state, carrier mobility, recombination... are not taken into account. And the more accurate $J_{SC}$ can be obtained by full space device optimization for PSCs [40], which would be carried out in the future theoretical and experimental works.
4. Conclusions
In conclusion, the microcavity PSCs using ultrathin Ag film electrode is adopted and they optical performance is systematically investigated. Compared to TCO based PSCs with conventional and inverted structures, the corresponding microcavity PSCs shows relatively poor light absorption and $J_{SC}$ due to the light transmittance limit of Ag film. When a TeO$_2$ optical coupling is introduced, PSCs with bottom-illuminated TeO$_2$(36nm)/Ag electrode obtain remarkably improved $J_{SC}$ and light absorption ability. And the top-illuminated microcavity PSCs exhibit better optical performance. Moreover, for inverted PSCs, an optical spacer with suited thickness results in redistribution of optical electric field and further improved light absorption and $J_{SC}$. The results show that both conventional and inverted PSCs with an optical microcavity could obtain comparable to or even better optical performance than TCO based PSCs, which demonstrates the possibility and provides a guideline to design and fabricate efficient TCO-free PSCs.

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