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Promising future of the perovskite solar cell presented from Prof. Lixin Xiao & Prof. Qihuang Gong’s research team at Peking University in collaboration with Prof. Zhaoxin Wu’s group at Xi’an Jiaotong University.

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A highly efficient mesoscopic solar cell based on CH$_3$NH$_3$PbI$_3$–xCl$_x$ fabricated via sequential solution deposition†

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Hybrid perovskite materials in the form of AMX$_3$ (A = CH$_3$NH$_3$; M = Pb$^{2+}$, or Sn$^{2+}$; and X = Cl$^-$, Br$^-$, or I$^-$) were first discovered by Weber and developed by Mitzi et al., and then CH$_3$NH$_3$PbI$_3$ or CH$_3$NH$_3$PbBr$_3$ was used as the dye-absorbing layer in a liquid dye-sensitized solar cell (DSC) reported by Miyasaka et al.$^{1–3}$ Following the pioneering work, the perovskites were used in solid-state solar cells to avoid the dissolution of perovskite in the presence of a liquid electrolyte. As a result, much higher power conversion efficiencies (PCEs) were achieved than those of liquid cells.$^{4–22}$ Recently, Snaith et al. found that the electron–hole diffusion lengths exceeded 1 $\mu$m for the mixed halide perovskite of CH$_3$NH$_3$PbI$_3$–xCl$_x$, while it was only 100 nm for the triiodide perovskite of CH$_3$NH$_3$PbI$_3$, showing the promising prospects of CH$_3$NH$_3$PbI$_3$–xCl$_x$.$^8$ The mixed halide perovskite CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ achieved 15.4% PCE through mix-vapor vacuum deposition to give a uniform perovskite film with a planar heterojunction.$^{10}$ However, vacuum deposition will greatly increase the cost of large-scale fabrication compared to the cost-effective solution process. Up to now, spin-coating deposition has been widely used for the fabrication of solution-based CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ cells, but only 7.6% PCE for the CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ cell containing the mesoporous TiO$_2$ layer.$^4$ While CH$_3$NH$_3$PbI$_3$ devices with shorter diffusion lengths achieved the efficiencies over 15% by two-step sequential solution deposition, with easier morphology control.$^{7,22}$ The morphology of the resultant perovskite film is very sensitive to the conditions during the spin-coating procedure, e.g., thickness of the compact TiO$_2$ layer, annealing time, annealing temperature and the thickness of the perovskite layer.$^{15}$ The morphology of the perovskite is crucial to the device performance, because the defects in perovskite crystallites and the interfaces may be the trap of charges, preventing them reaching the electrodes. Therefore, it is necessary to improve the morphology of the CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ cell through the solution-based method.

To further improve the photovoltaic performance of mixed halide perovskite of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ via the solution process, in this work, we successfully figure out the feasible compositions of the precursor for the CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ perovskite by two-step sequential deposition, permitting much easier morphology control. A mixture precursor of PbI$_2$ and PbCl$_2$ is more promising for the preparation of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ than pure PbCl$_2$, due to the poor solubility of pure PbCl$_2$. The device performance reaches 11.7%, which is the highest efficiency for CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ cell via the solution process containing a mesoporous TiO$_2$ layer based on our knowledge, much higher than 4.8% for the device fabricated via spin-coating deposition.

The CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ perovskite was first reported by Snaith et al. by using a mixture of CH$_3$NH$_3$I and PbCl$_2$ with a molar ratio of 3 : 1 via spin-coating deposition (Scheme 1b).$^{4,5,8}$ Following this reaction, we first tried to use saturated (0.5 M) PbCl$_2$ as the precursor in the two-step sequential deposition, and spin-coated it on the mesoporous TiO$_2$ film, and then dipped into CH$_3$NH$_3$I

$$\text{2 CH}_3\text{NH}_3\text{I} + \text{PbCl}_2 \rightarrow 2 \text{ CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x}$$  

(a)

$$\text{3 CH}_3\text{NH}_3\text{I} + \text{PbCl}_2 \rightarrow \text{ CH}_3\text{NH}_3\text{PbI}_x\text{Cl}_{3-x} + \text{ CH}_3\text{NH}_3\text{I} \uparrow + \text{ CH}_3\text{NH}_3\text{Cl} \uparrow$$  

(b)

Scheme 1  The reactions for CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$.  

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solution to form perovskite on site. Unfortunately, the absorption of the resultant film was very weak. It might be due to the poorer solubility of PbCl2 than that of PbI2 in dimethylformamide (DMF), because high concentration (at least 1 M) of the precursor is very important to obtain high loading in the mesoporous TiO2 film for high device performance.7 However, in the presence of additives, e.g., PbI2 or CH3NH3I, the solubility of PbCl2 can significantly increased due to the common ion effect.15,31 In addition, the higher formation energy of chlorine incorporation into the perovskite matrix than that of iodine might also be the reason.26 Therefore, we changed the precursor to a mixture of 0.5 M PbCl2 and 0.5 M PbI2 (molar ratio 1 : 1) according to the reaction of Scheme 1a, and followed the two-step sequential deposition to give Film a with the color changing from chartreuse to dark brown, indicating the formation of the perovskite. From the reaction formula given below, it could also be inferred that Scheme 1a tends to give less byproducts compared to Scheme 1b. The excess methylammonium iodide and chloride are assumed to be lost via evaporation during the annealing process.4 Less byproducts may leave fewer pin-holes in the perovskite layer during the annealing process.15 As comparison, the resultant film formed by using PbCl2 as the precursor (Scheme 1b) is referred to as Film b. The illustrations of different fabrication procedures for CH3NH3PbI3-xClx layers are shown in Fig. 1.

The structures of the resultant perovskite films were investigated via X-ray diffraction (XRD) as shown in Fig. 2a. The structure of the synthesized perovskite is consistent with tetragonal phase structures reported in the previous reports.23–25 Strong peaks at 14.03° and 27.52°, corresponding to the (110) and (220) planes, confirm the formation of a tetragonal perovskite structure with lattice parameters a = b = 8.84 Å and c = 12.57 Å. The signals of Film b are much weaker than those of Film a, indicating that more perovskite crystallites formed in mesoporous TiO2 by the mixture of PbI2 and PbCl2 than pure PbCl2 as the precursor. The composition of Film a was confirmed by the energy-dispersive X-ray (EDX) spectrum as shown in Fig. S1 (ESI†). The elemental mapping analysis of the surface confirms that the resultant perovskite of Film a is a mixed halide CH3NH3PbI3-xClx with approximately x ≈ 0.26. The images of Pb, I and Cl also show that the perovskites are well distributed. The absorption spectra of the two perovskite films are shown in Fig. 2b. Film a has strong broadband absorption in the visible region from 400 nm to 800 nm, on the contrary, Film b has rather poor absorption, indicating insufficient perovskite filling in the porous TiO2 layer. These results indicate that using the mixture of PbI2 and PbCl2 as the precursor is an effective way to form the mixed halide perovskite of CH3NH3PbI3-xClx, following Scheme 1a.

To further evaluate the differences in the resultant CH3NH3-PbI3-xClx perovskite layers between two-step sequential deposition and spin-coating deposition, we also fabricated another perovskite layer via spin-coating the mixture of CH3NH3I, PbCl2 and PbI2 (molar ratio 2 : 1 : 1) also following Scheme 1a for comparison (hereafter referred to as Film c). The morphology of Film a, Film b and Film c was measured by both scanning electron microscopy (SEM) and atomic force microscopy (AFM) as shown in Fig. 3.
By using the mixture of PbI₂ and PbCl₂ as the precursor (Film a), the perovskite via two-step sequential deposition did not only penetrate deeply into the mesoporous TiO₂, but also grew into crystallites to cover the TiO₂ layer with an in-plane grain size of 300–350 nm as shown in Fig. 3a, and the grain size has been proved to be suitable with a strong light scattering effect to further enhance the light absorption.⁶⁶ On the contrary, there were almost no more perovskite crystallites on top of the mesoporous TiO₂ for Film b fabricated via two-step sequential deposition by using PbCl₂ as the precursor as shown in Fig. 3b, indicating insufficient pore filling in the mesoporous TiO₂ layer. This might be one of the possible reasons for the absorption difference by using different precursors. For Film c, the SEM images (Fig. 3c) showed that no continuous perovskite capping layer was formed on top of the mesoporous TiO₂, although there was penetration into the mesoporous TiO₂ layer. The above results indicate that the morphology of the perovskite layer fabricated via two-step sequential deposition is easier to control compared with via spin-coating deposition. The surface morphology of the three films was also investigated via AFM images. As a result, the crystalline arrangement in Film a formed a continuous microstructure consistent with the SEM image, the absorption of incident light was enhanced due to the presence of the crystalline perovskite capping layer and the light scattering effect, which have also been proved to be an effective way in DSCs.³²,³⁷ These results could be proved by the cross-section image (Fig. 3d) with elemental mapping (Fig. S2, ESI†) of Film a. It could be clearly identified that the perovskite not only formed a continuous capping layer, but also penetrated well into the mesoporous TiO₂ film. The perovskite pore-filling should improve the device performance because higher electron densities can be sustained in the TiO₂ layer, increasing electron transporting rates as previously reported.²⁸ To further evaluate the interfacial properties of TiO₂/pervoskite, the transmission electron microscopy (TEM) image (Fig. 3c) was obtained from the scratch from Film a. The image reveals the formation of the CH₃NH₃PbI₃–Cl perovskite thin film on the TiO₂ surface, which prohibits the direct contact between TiO₂ and hole transporting material (HTM).

The experimental details of device fabrication are given in the ESI†. Devices A and B correspond to Film a and Film c, respectively. Devices were measured under a standard AM 1.5 illumination of 100 mW cm⁻². The J–V curves are shown in Fig. 4a. The incident photon to current conversion efficiency (IPCE) was measured as shown in Fig. 4b.

### Table 1 Photovoltaic performances of the hybrid perovskite solar cells

<table>
<thead>
<tr>
<th>Device</th>
<th>Process</th>
<th>Voc [V]</th>
<th>Jsc [mA cm⁻²]</th>
<th>FF</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Sequential</td>
<td>1.04</td>
<td>17.2</td>
<td>0.65</td>
<td>11.7</td>
</tr>
<tr>
<td>B</td>
<td>Spin-coating</td>
<td>0.86</td>
<td>9.4</td>
<td>0.59</td>
<td>4.8</td>
</tr>
<tr>
<td>Ref. 10</td>
<td>Vacuum</td>
<td>1.07</td>
<td>21.5</td>
<td>0.67</td>
<td>15.4</td>
</tr>
<tr>
<td>Ref. 4</td>
<td>Spin-coating</td>
<td>0.80</td>
<td>17.8</td>
<td>0.53</td>
<td>7.6</td>
</tr>
</tbody>
</table>

Compared with Device B, the IPCE of Device A is over 60% between 400 to 700 nm, and the highest value is nearly 80% at around 500 nm, matching the stronger absorption region of the perovskite layer. The PCE of Device A is up to 11.7%, with a Jsc of 17.2 mA cm⁻², a Voc of 1.04 V, and a FF of 0.65, which is the highest efficiency for CH₃NH₃PbI₃–Cl via the solution process containing a mesoporous TiO₂ layer based on our knowledge, much higher than that of 7.6% obtained via the spin-coating process with the mesoporous TiO₂ layer as reported listed in Table 1.⁴ The corresponding Device B showed a Jsc of 9.4 mA cm⁻², a Voc of 0.86 V, a FF of 0.59 and 4.8% PCE (Fig. 4a), a much lower PCE than that of the Device A fabricated via two-step sequential deposition. The improvement of photovoltaic performances may be mainly ascribed to the different morphology of the two devices. Compared with Device A, there is 0.18 V decrease in the Voc of Device B because of the direct contact between the uncovered TiO₂ and the p-type HTM due to the absence of the perovskite capping layer, resulting in the charge recombination between the TiO₂ and HTM.¹⁵,²₈,²⁹ Besides, the absence of the perovskite capping layer might lead to lower absorption, resulting in lower Voc. It should be noted here that the lower PCE than 15% for CH₃NH₃PbI₃ via two-step sequential deposition might be due to the lower solubility of PbCl₂ than that of PbI₂ in the solvent of DMF. High concentration should be crucial to the growth of perovskite crystallites as reported in the case of CH₃NH₃PbI₃ via two-step sequential deposition.⁷ This could be also supported by the lower PCEs for CH₃NH₃PbI₃–Cl via the solution process than that via vacuum deposition (sufficient chlorine source). Compared to the CH₃NH₃PbI₃–Cl cell with 15.4% PCE fabricated via vacuum deposition, the Voc and FF of the spin-coated CH₃NH₃PbI₃–Cl cells are significantly lower, due to the difficulty in controlling the morphology of the perovskite crystallites formed via a spin-coating process, leading to the lower PCE of 7.6%. While Device A fabricated via two-step sequential deposition is an effective method to reduce the Voc and FF losses caused by the morphology defects of CH₃NH₃PbI₃–Cl perovskite. Further work should be focused on optimizing the conditions to control the morphology of the perovskite capping layer to further increase the lower Voc caused by the low solubility of PbCl₂ as mentioned above.

In conclusion, we introduce two-step sequential solution deposition for the fabrication of the CH₃NH₃PbI₃–Cl mesoscopic solar cell. The mixture of PbI₂ and PbCl₂ is used rather than pure PbCl₂ as the precursor to ensure high loading in the mesoporous TiO₂ film, with easy morphology control, which results in a great enhancement of the light absorbance for the device and suppressing the electron hole recombination by separating the bare TiO₂ and the HTM layer. As a result, 11.7% PCE for the device has been achieved with a Jsc of 17.2 mA cm⁻²,
Notes and references

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