Semitransparent and flexible perovskite solar cell with high visible transmittance based on ultrathin metallic electrodes

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We have fabricated semitransparent and flexible indium-free perovskite solar cells (PeSCs) with high visible transmittance employing two kinds of composite ultrathin metallic electrodes, MoO$_3$/Au and MoO$_3$/Au/Ag/MoO$_3$/Alq$_3$, as the bottom and top electrodes, respectively. These electrodes show superb electrical conductivity, excellent mechanical robustness, and high optical transparency which are quite suitable for semitransparent and flexible PeSCs. An overall power conversion efficiency (PCE) of 6.96% and an average visible transmittance of 18.16% in the wavelength range of 380–790 nm were achieved. Furthermore, the devices maintained 71% of their initial PCE after 1000 bending cycles with a bending radius of 4 mm.

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Perovskite solar cells (PeSCs) have attracted tremendous attention since the first Letter of a perovskite-sensitized solar cell with an efficiency of 3.8% in 2009 [1]. The first solid-state PeSCs with an efficiency of 9.7% were reported in 2012 by using a more rational design of the cell architecture [2], and the efficiency has risen to 21.6% in just four years [3–5]. In addition to the high efficiency, the PeSCs show the advantages of being mechanically flexible, low-temperature solution-processable, and low in cost [6–8]. Hence, PeSCs are the most promising choice for semitransparent and flexible solar cells [9–12]. In order to obtain PeSCs with high visible transmittance, the opaque top electrode of the device must be replaced by electrode meeting stringent technical constraints such as high optical transparency in the visible wavelength range of 380–790 nm, quite low sheet resistance and bendable (capable for flexible device). Most importantly, the electrode could be used as the top electrode without damaging the underlying layers, since the perovskite films are sensitive to the temperature and solvent. So far, an electrode meeting these criteria has not been demonstrated. The required wet chemical and annealing steps for the silver nanowires [13,14] or conductive polymers such as PEDOT: PSS [12] cannot easily be realized on top of the device without damaging the underlying layers. Preparation and deposition of electrodes, including carbon nanotubes [15,16] and graphenes [17,18] as the top electrodes, are expensive and complicated. In comparison, ultrathin metallic layers [10,19,20] fabricated by thermal evaporation are ideal options of the transparent top electrodes because they are not only process-compatible to the underlying layers, but also show high visible optical transparency, superb electrical conductivity, intrinsically mechanical robustness, and high-temperature stability.

In the case of the bottom electrode, indium-tin-oxide (ITO), which was the most commonly used transparent and conductive bottom electrode in present PeSCs, has increased the overall expenses of the device, and the scarcity of indium reserves can be a potential barrier to large-scale cost-effective manufacturing [21,22]. In addition, the brittleness of ITO in nature which made it prone to crack under repeated bending has limited the future development of PeSCs, particularly in a flexible format [9,23–26]. Therefore, developing a simple and effective method to obtain a valid alternative bottom transparent electrode for ITO is imminent. Among all attempts to design indium-free and flexible PeSCs [23,27–29], an ultrathin and high-conductivity metallic film has been considered as one of the most ideal alternative electrodes [30,31]. Although an ultrathin metallic film with a thickness of less than 10 nm shows a high optical transparency, the thermally evaporated metallic film follows the Volmer–Weber growth mode [30,32] and results in a non-conductive film with a rough surface morphology.

In our experiments, nucleation-inducing seed layers of molybdenum trioxide (MoO$_3$) and Au have been employed to modulate the surface energy and optimize the growth conditions of metal films to form continuous and conductive ultrathin metallic electrodes [33,34]. Two layers of high refractive MoO$_3$ have been introduced as dielectric layers to improve light transmittance [35,36]. An organic capping of Alq$_3$ film has been used to enhance the light incoupling [37]. Finally, ultrathin Au and Ag films have been optimized as MoO$_3$ (3 nm)/Au (10 nm) and MoO$_3$ (3 nm)/Au (1 nm)/Ag...
(7 nm)/MoO3 (5 nm)/Tris-8-hydroxyquinoline aluminum (Alq3) (50 nm) (DMD), and can be used as the bottom and top electrodes to prepare efficient, ITO-free, semitransparent and flexible PeSCs, respectively (Fig. 1). The PeSCs achieved a considerable PCE of 6.96% with an average light transmittance (AVT) of 18.16%, which is the highest among reported PeSCs with similar AVT, to the best of our knowledge [20,36,38,39]. By replacing ITO with ultrathin metallic electrodes, the flexibility of the device was increased substantially as it could maintain 71% of its initial PCE after 1000 bending cycles with a bending radius of 4 mm.

The structure of the PeSCs was photore sist (NOA63, Noland Optical Adhesive 63)/MoO3/Au/PEDOT: PSS/CH3NH3PbI3·XClX/PCBM/DMD top electrode (Fig. 1). The experimental procedures are as follows. The photore sist, NOA63, was spin-coated at a rotation speed of 8000 rpm for 30 s onto a pre-hydrophobic treated Si wafer and then cured by UV-ozone treatment. Then the NOA63 film with an AVT of 91% was peeled off from the Si wafer and transferred into a vacuum thermal evaporation chamber to grow 3 nm MoO3 and 10 nm Au films in sequence as bottom electrodes. After that, the sample was transferred into a nitrogen glove box to maintain 71% of its initial PCE after 1000 bending cycles with a bending radius of 4 mm.

Au and the NOA63 substrate. The sheet resistance was decreased greatly from 15 Ω/sq for barely Au (10 nm) to 9 Ω/sq for the MoO3 (3 nm)/Au (10 nm) as well. After annealing at 95°C for 110 min, the sheet resistance of the MoO3 (3 nm)/Au (10 nm) shows negligible variation from 9 to 10 Ω/sq. In terms of mechanical flexibility, the MoO3 (3 nm)/Au (10 nm) on the NOA63 film could retain its low resistance (~110 Ω/sq) after 1000 bending cycles with a bending radius of 4 mm, suggesting its potential application as a bottom electrode in the flexible PeSCs.

Figure 2(b) shows the transmittance curves and sheet resistances of the top electrodes. As it could be seen, the performance of electrodes was heavily optimized by introducing the DMD structure. The MoO3 (3 nm)/Au (1 nm)/Ag (7 nm)/MoO3 (5 nm)/Alq3 (50 nm) achieved an AVT of 89.65% which is much better than that of Ag (7 nm) (49.59%), Au (1 nm)/Ag (7 nm) (64.80%) and MoO3 (3 nm)/Au (1 nm)/Ag (7 nm) (78.50%). In addition, the sheet resistance of Ag (7 nm) was reduced by several orders of magnitude from >1 MΩ/sq to around 35 Ω/sq [Au (1 nm)/Ag (7 nm)] by introducing a ultrathin Au layer as a seed layer for Ag and further reduced to 16 Ω/sq [MoO3 (3 nm)/Au (1 nm)/Ag (7 nm)] by introducing a MoO3 layer which can worked as a seed layer for Au as well.

The structure and composition of CH3NH3PbI3·XClX film were studied using a scanning electron microscopic (SEM, JSM-7500F; JEOL, JEOL Ltd., Tokyo, Japan), x-ray diffraction (XRD, Shimadzu XRD-6000), and UV-vis absorbance spectroscopy (UV-2550, SHIMADZU). As shown in Fig. 3(a), the perovskite film exhibits a dense-grained, extremely uniform, continuous, and pinhole-free morphology with grain sizes up to micrometer scale. The XRD peaks [Fig. 3(b)] located at 14.4°, 28.72°, 43.5°, and 59.14° in the entire 2θ ranges are assigned to (110), (220), (330), and (440) planes of tetragonal CH3NH3PbI3·XClX, respectively [1,45,46]. There was no intense and characteristic XRD peak of PbCl2 observed at 22.68°, indicating the complete reaction of PbCl2 and MAI and the formation of a pure CH3NH3PbI3·4ClX phase [47].

The cross-sectional SEM of the PeSC was shown in Fig. 4(a). As it could be seen, there are little to no observable interdiffusion between layers and the thickness of the perovskite film was about 230 nm. Figure 4(b) illustrates visual light
absorbance and transmittance spectra of perovskite film and the transmittance spectrum of the complete PeSCs. The perovskite films show a strong typical absorption spectrum, as reported, suggesting strong light absorption [47,48]. The highest transmittance of the perovskite film is found to be about 71.54% at 790 nm. The average AVT of 12 PeSCs was evaluated to be 18.16%.

Figure 4(c) shows photographs of PeSCs as corroborative evidences of the high AVT and mechanically flexible of the device.

Figure 5 compares the current density-voltage (J–V) characteristics of the PeSCs scanned in two different directions (forward and reverse scans) under illumination with simulated AM 1.5 G with a light intensity of 100 mW cm\(^{-2}\) from both the top and bottom sides. They demonstrated negligible current hysteresis, so we studied J–V characteristics scanned in forward directions as a representative below. The precise average photovoltaic parameters of 12 PeSCs were summarized in Table 1. The best performance PeSCs based on the ITO bottom electrode achieved an AVT value of 21.96%, short-circuit photo-currents (\(J_{SC}\)) of 18.77 and 18.54 mA cm\(^{-2}\), open circuit voltages (\(V_{OC}\)) of 0.950 and 0.952 V, fill factors (FF) of 70.18 and 68.31%, and PCE of 12.46 and 12.06% for the top and bottom illumination sides, respectively. By replacing the brittle and expensive ITO with robust and flexible ultrathin metallic film, the best performance PeSCs show the \(J_{SC}\), \(V_{OC}\), FF, and PCE of 13.86 and 12.61 mA cm\(^{-2}\), 0.827 and 0.813 V, 60.72 and 58.23%, and 6.96 and 5.97% obtained from the top and bottom illumination sides, respectively.

As all layers of the PeSCs show great robustness and bendability [9,49], the device manifested superior flexibility and mechanical endurance. In order to verify the high flexibility of the PeSCs, bending tests were performed, taking into account the bending radii and cycle. As shown in Fig. 6(a), the PCE of PeSCs exhibited no significant decrease at the first bending cycle, even with an extremely small bending radius of 4 mm, retaining 99.2% of the original PCE. The variation of the device performance with bending cycles was shown in Fig. 6(b). The J–V curve of the device after 1000 bending cycles with a bending radius of 4 mm was shown in Fig. 5(a) (green curve with diamonds and orange curve with stars).

Table 1. Average Photovoltaic Parameters of 12 PeSCs Based on Different Bottom Electrodes Illuminated from both the Top and Bottom Sides

<table>
<thead>
<tr>
<th>Electrode</th>
<th>(V_{OC}) (V)</th>
<th>(J_{SC}) (mA cm(^{-2}))</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>AVT (%)</th>
</tr>
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<tbody>
<tr>
<td>ITO</td>
<td>0.943(^a)</td>
<td>18.61(^a)</td>
<td>69.87</td>
<td>12.26(^a)</td>
<td>21.76</td>
</tr>
<tr>
<td>ITO</td>
<td>0.948</td>
<td>18.48</td>
<td>68.07</td>
<td>11.92</td>
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</tr>
<tr>
<td>MoO(_3)/Au</td>
<td>0.825(^a)</td>
<td>13.81(^a)</td>
<td>60.54(^a)</td>
<td>6.90(^a)</td>
<td></td>
</tr>
<tr>
<td>MoO(_3)/Au</td>
<td>0.806</td>
<td>12.45</td>
<td>58.13</td>
<td>5.83</td>
<td>18.16</td>
</tr>
<tr>
<td>After bending</td>
<td>0.800(^a)</td>
<td>10.87(^a)</td>
<td>57.20(^a)</td>
<td>4.97(^a)</td>
<td></td>
</tr>
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\(^a\)Illuminated from the top side.
PeSCs achieved a considerable AVT of 18.16% and a PCE of 6.96% which is the highest among the reported semitransparent, flexible, and ITO-free PeSCs, to the best of our knowledge. Furthermore, the PeSCs show super flexibility as it could maintain 71% of their original efficiencies after 1000 bending cycles with a bending radius of 4 mm.

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**REFERENCES**