We have fabricated organic-inorganic hybrid perovskite solar cell that uses a Ti/Au multilayer as cathode and does not use electron transport materials, and achieved the highest power conversion efficiency close to 13% with high reproducibility and hysteresis-free photocurrent curves. Our cell has a Schottky planar heterojunction structure (ITO/PEDOT:PSS/perovskite/Ti/Au), in which the Ti insertion layer isolate the perovskite and Au layers, thus proving good contact between the Au and perovskite and increasing the cells’ shunt resistance greatly. Moreover, the Ti/Au cathode in direct contact with hybrid perovskite showed no reaction for a long-term exposure to the air, and can provide sufficient protection and avoid the perovskite and PEDOT:PSS layers contact with moisture. Hence, the Ti/Au based devices retain about 70% of their original efficiency after 300 h storage in the ambient environment.
in Table 1. It can be found that in the device with Au cathode, the PCE is only 6.3% with poor fill factor (FF, ~43%) and small open circuit voltage (Voc, 0.65 V). After the insertion of Ti layer (5 nm), an obvious PCE enhancement is observed, with the FF, Voc and short circuit current (Jsc) elevated to ~51%, 0.89 V and 23.64 mA/cm², respectively. When the Ti film thickness raises to 10 nm, the highest PCE approaching 13% is achieved with the Jsc up to 24.38 mA/cm². It demonstrates that the Ti/Au multilayer can effectively improve the device performance.

![Energy band alignment of the device is shown in Fig. 1(c). The work functions of PEDOT:PSS (−5.3 eV) and Au (−5.1 eV) are both close to the valence band edge of MAPbI₃ (−5.4 eV), which causes the carriers recombination at the electrodes and limits the charge collection. This is the main reason for the poor photovoltaic parameters of the ITO/PEDOT:PSS/MAPbI₃/Au devices. In contrast, inserting a layer of Ti thin film can effectively raise the voltage and block the holes without affecting the electrons collection of cathodes, since the work function of Ti is higher than that of PEDOT:PSS by about 1 eV and slightly lower than the conduction band edge of MAPbI₃.

Accordingly, the maximum Voc and Jsc of the ITO/PEDOT:PSS/MAPbI₃/Ti/Au devices have reached 0.89 V and 24.38 mA/cm² (Table 1), close to those of the devices with ETM multilayer films. To our delight, there are only negligible changes in our sample's photocurrent density with reverse and forward scan, even better than the cells with ETM (PCBM/C₆₀/BCP). Therefore, the Ti insertion layers have not only improved significantly the ETM-free device PCE, but also achieved high repeatability and hysteresis-free photocurrent curves.

### Table 1. The best ETM-free solar cell photocurrent parameters based on different cathodes.

| Sample          | Jsc (mA/cm²) | Voc (V)  | FF       | PCE     |
|-----------------|--------------|----------|----------|---------|
| Ti (5 nm)/Au    | 23.64        | 0.89     | 51.19%   | 10.77%  |
| Ti (10 nm)/Au   | 24.38        | 0.89     | 59.49%   | 12.91%  |
| Ti (20 nm)/Au   | 18.73        | 0.79     | 33.12%   | 4.90%   |
| Au              | 22.47        | 0.65     | 43.11%   | 6.30%   |

**Figure 1.** (a) Schematic drawing showing the vertical structure of the ITO/PEDOT:PSS/MAPbI₃/Ti/Au devices; (b) J-V of the devices under 1.5 sun illumination with Au and Ti/Au cathodes, and with different Ti film thickness of 5, 10 and 20 nm; (c) Energy level diagram of the discussed solar cell which shows the charge separation process. The positions of the energy levels are according to ref. 10. (d–g) Histograms of short-circuit current density, open-circuit voltage, fill factor and power conversion efficiency of 24 cells for the devices with Ti(10 nm)/Au and Au cathode, respectively. (h) J-V curves with different scanning direction at a sweeping rate of 0.05 V/s under AM 1.5 G one sun illumination.
It is worthy of note that the device performance has suddenly decayed when the Ti insertion layer thickness reaches 20 nm (Fig. 1(a) and Table 1). The PCE was less than 5% and the FF was close to 30%, which was even lower than those of the device using Au cathode. The reason will be discussed later.

Series resistor ($R_s$) and shunt resistor ($R_{sh}$) of the ETM-free devices with different cathodes (Au(80 nm), Ti (10 nm)/Au(80 nm) and Ti(60 nm)) have been also measured, and shown in Supplementary Figure S1. In the devices with Au, Ti/Au and Ti cathodes, the $R_s$ are 1.39 $\Omega$/cm$^2$, 8.94 $\Omega$/cm$^2$ and 122.26 $\Omega$/cm$^2$ and the $R_{sh}$ are 68.31 $\Omega$/cm$^2$, 6409.8 $\Omega$/cm$^2$ and 23558.4 $\Omega$/cm$^2$, respectively. This indicates that the $R_{sh}$ can be improved by two orders of magnitude with a proper thickness (~10 nm) of the Ti films, while the influence of the $R_s$ is limited.

As an ideal solar cell should have a small $R_s$ and a larger $R_{sh}$, the giant $R_{sh}$ is beneficial for the devices to obtain excellent performance. However, with the increase of the Ti films thickness, the $R_s$ increases rapidly. When the Ti cathode thickness reaches 60 nm, the $R_s$ is also increased by 100 times. Because of increase of the internal resistance, the photovoltaic parameters of the cell with 20 nm Ti insertion layer have been greatly reduced and even less than the device with Au cathode.

Scanning electron microscopy (SEM) images for MAPbI$_3$/Au, MAPbI$_3$/Ti/Au and MAPbI$_3$ films are shown in Fig. 2, respectively. In consistence with other works$^{16,17}$, the MAPbI$_3$ was a polycrystalline film composed of grains with size ~300 nm. From the Fig. 2(b) and (c), the Au films (10 nm and 20 nm) were also composed of nanoparticles with a pin-hole free surface. Moreover, from the cross section SEM shown in the Fig. 2(d), it can be found that there is large density of voids at the interface between the Au and MAPbI$_3$ films. These indicate that Au metal has a poor wettability on the surface of MAPbI$_3$, and cannot form a uniform thin film. However, after the deposition of Ti and Au on MAPbI$_3$ in turn, a firm and compact film is obtained as shown in Fig. 2(e) and (f), which suggests that the

![Figure 2](image-url)
Ti insertion layer can improve the wettability of Au on the surface of MAPbI$_3$. In other words, the Ti layers can help to form a good contact between the MAPbI$_3$ films and metal Au electrode, which can improve the charge collection and eliminate the void-inducing the charge accumulation. This is also one of the important reasons for the significant improvement in the related device performances, such as $J_{sc}$ and FF.

Many works have reported the existence of a large density of charge traps in MAPbI$_3$ films, especially in the grains surface and interface, which can be effectively passivated by PCBM and C$_60$. In order to investigate the influence of different cathode materials (Ti, Au and PCBM) on the trap states, the corresponding photoluminescence (PL) emission spectra were measured and shown in Fig. 3(a). Compared with the standard MAPbI$_3$ sample spun on ITO glass, the Ti and PCBM films can cause blue-shift in the PL emitting wavelength of 12 and 10 eV respectively, while the Au film bring a blue-shift of about 4 eV. Based on the work of Huang’s group, the trap states can cause a red-shift of PL spectrum. Therefore the PL results indicate that the Ti insertion layer can reduce the density of charge traps in the surface/interface, which is more effective than PCBM. On the contrary, the contact between MAPbI$_3$ and Au has brought more trap states than the standard sample.

The voids at the interface between Au and MAPbI$_3$ may induce accumulation of the charged ions or vacancies at the electrode interfaces, and then cause the ionic migration which may induce the photocurrent hysteresis in the ITO/PEDOT:PSS/MAPbI$_3$/Au devices. Moreover, the charge traps in MAPbI$_3$ films, which can trap carriers and cause recombination, are also responsible for the photocurrent hysteresis. Our results have demonstrated that with a good contact, the Ti/Au film can also effectively reduce the density of charge traps at the interface between the cathode and MAPbI$_3$. Therefore, there is no hysteresis in the ETM-free devices with ITO/PEDOT:PSS/MAPbI$_3$/Ti/Au structure, as show in Fig. 1(h). Moreover, since the Ti insertion layers can eliminate the voids and traps, the interface morphology between the cathode and perovskite has a good reproducibility. Meanwhile, as the spin-coating/evaporation of ETMs is omitted, the fabrication factors that affect the devices performance are also reduced. Therefore, the ETM-free device with Ti/Au cathode has shown a high repeatability, as shown in Fig. 1(d–g).

Finally, we have investigated the stability of various device structures without encapsulation in an ambient environment at 30–20°C and with ~50% humidity, as shown in Fig. 3(b). (The time dependent photocurrent curves for each device are given in Supplementary Figure S2) The PCE of devices with PCBM/C$_60$/Au and Au cathodes decays rapidly in air and almost drops to zero within 30 h. The degradation mechanisms occurring may be due to these reasons: (1) the absorption of oxygen/water by the PCBM, (2) the acidic and hygroscopic properties of PEDOT:PSS and (3) incomplete coverage of the perovskite film by the Au cathode. In contrast, the device using the Ti/Au cathode discards the PCBM as an ETM and ensures a perfect contact between the perovskite and metal cathode, providing sufficient protection and avoiding the perovskite and PEDOT:PSS contact with the air. Moreover, it must be highlighted that Ti in direct contact with MAPbI$_3$ showed no reaction for a long-term exposure to moisture and oxygen, what is different from other common metal cathodes, such as Au, Al, Ag and Cu. These make the PCE of the Ti/Au based ETM-free device remain above 70% of the initial value even after 300 h of storage in the ambient environment.

In conclusion, high-performance ETM-free PSCs using Ti/Au multilayer cathode have been demonstrated. The Ti insertion layer is a very simple and effective approach to increase the cell’s $R_{sh}$, and improve the interface morphology between Au and perovskite. Moreover, our cells has also shown hysteresis-free photocurrent curve, high reproducibility and high stability in the ambient environment, due to the passivation of charge traps and the...
exclusion of voids at the interface. As a result, a high PCE of ~13% has been obtained and retain about 9.2% after 300 h storage in air at room temperature. This result not only reveals the promising applicability of Ti/Au multilayer in the ETM-free PSCs, but also affords a novel approach for high performance and decently stable PSCs.

**Methods**

Device fabrication and characterization. PEDOT:PSS (Clevious P VP AI 4083) was spin-coated on clean ITO substrates at a speed of 3000 revolutions per minute (r.p.m.) for 60 s, and then annealed at 120 °C for 30 min. The MAPbI3 films (~350 nm) were fabricated by two-step spin-coating procedures in a nitrogen-filled glovebox (<0.1 ppm O2 and H2O). PbI2 (99%, Aldrich, 650 mg/ml in DMF) and MAI (synthesized with meth-yamine and hydroiodic acid15, 70 mg/ml in 2-propanol) were spun on PEDOT:PSS substrates at 6000 r.p.m. for 35 s respectively, followed by thermal annealing at 100 °C for 1 h. Finally, the “ITO/PEDOT:PSS/MAPbI3/Ti/Au” devices were finished by thermal evaporation of metal cathode layers (Ti and Au) in turn, and “ITO/PEDOT:PSS/MAPIbI3/PCBM/C60/BCP/Au” devices were finished by spin coating of PCBM (99%, Nano-c, 20 mg/ml, 6000 r.p.m.) and thermal evaporation of C60 (30 nm) (99%, Nano-c), BCP (6 nm) (99%, Taiwan) and Au in turn.

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**Author Contributions**

T.S., J.C., and Y.Q., contributed to the experiment design, fabricated the devices, wrote the manuscript and interpreted the results. J.Z., X.L., B.Z., and H.C., characterized the perovskite solar cells properties using the SEM and electrochemical impedance spectroscopy (EIS). All authors discussed the results and commented on the manuscript.

**Additional Information**

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