Reverse Diffusion of Atomically Engineered Hole-Extraction Materials between Crystal Grains for Achieving Efficient

Perovskite Solar Cells



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Introduction

Organic-inorganic hybrid lead halide perovskite solar cells (PVSCs) experienced rapid progress in improving their power conversion efficiencies (PCEs) from 3.8 % to 22.1 % within



seven years. However, the interfacial properties as well as the scope of contacting materials to perovskites remain less explored, since the commonly used hole extraction materials (HEMs) are dominant by 2,2,7,7-tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene (Spiro-OMeTAD) and its analogous containing OMeTAD moieties. They usually require additive doping to improve the conductivity, resulting in the complicated device processing and detriment to the device stability, which are drawbacks adding to PVSCs.

Herein we present two HEMs based on a tetraphenyl core and arylamine periphery groups, namely, TPP-OMeTAD and TPP-SMeTAD. Further characterizations shows both HEMs enable good power conversion efficiency (PCE) in p-i-n perovskite solar cells. It is interesting to point out that with only one atom difference at the periphery group, devices based on TPP-SMeTAD HEM shows PCE of 16.6% with negligible hysteresis, which is 14% averagely higher than that of TPP-OMeTAD based devices (PCE of 14.6%). Moreover, unlike the traditional PVSC architecture, those two HEMs possessing marginal solubility in DMF can reversely diffuse into the crystal boundaries during two-step fabrication of perovskite uplayer, resulting in a gradient HEM distribution in and under perovskite layer. It facilitates the improved holes collection and reduced recombination loss.



Fig. 3 (a) The architecture schematic of the inverted perovskite devices and (b) Energy level diagram of perovskite devices based on TPP-OMeTAD and TPP-SMeTAD as HEMs. (c) J-V curves of the best performance devices based on TPP-SMeTAD OMeTAD and TPP-SMeTAD as HEMs. (d) External quantum efficiency spectra (EQE) spectrum of PVSCs based on TPP-SMeTAD OMeTAD and TPP-SMeTAD as HEMs.

Table 1. Current Density-Voltage (*J-V*) Curves of PVSCs applying TPP-OMeTAD and TPP-SMeTAD as HEMs under AM 1.5G Illumination (100 mW·cm⁻²)

HEM	Scan direction	V _{oc} [V]	J _{sc} [mA cm⁻²]	FF	PCE [%]	Cal. J _{sc} [mA cm ⁻²]
TPP-OMeTAD	Forward	0.98	18.58	0.71	13.0	17.42



Fig. 4 A schematic diagram of the deposition method; the orange dash line represents HEMs allocating along the grain boundary.

Conclusions

In conclusion, two triphenylamine-based small molecule HEMs for PVSCs devices were synthesized by tuning the periphery group, namely, TPP-OMeTAD and TPP-SMeTAD. Significantly improved PCE was noticed when replacing O-atom with S-atom at the periphery group, from 14.6% to 16.6%, which might attribute to a larger atomic radius of S-atom (softer Lewis base) comparing with O-atom so that a stronger interaction with Pb²⁺ ion (soft Lewis acid) in perovskite film. Moreover, a heterojunction structure was proposed and verified that HEM molecules existed in the gap between grains in perovskite film, which enhanced the hole collection capability and reduced the recombination loss. Our work can provide new insights on the molecule engineering of hole-collection materials that enables efficient organic-inorganic hybrid PVSCs.





Fig. 2 (a) SIMS profiles showing I (black), and S (red) elements distribution in perovskite film. (b) XRD patterns of perovskite films fabricated atop of TPP-OMeTAD (red) and TPP-SMeTAD (black); asterisks indicate perovskite peaks and hash marked peaks belong to ITO. (c), (d) Top view of the perovskite film based on TPP-OMeTAD and TPP-SMeTAD as HEMs, respectively. Contact angle of water on (e) TPP-OMeTAD and (f) TPP-SMeTAD.

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Notes and references

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