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Perovskite-organic hybrid tandem solar cells using a nanostructured perovskite layer as the light window and a PFN/doped-MoO₃/MoO₃ multilayer as the interconnecting layer†

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In this study, we present a two-terminal perovskite (PVSK)-organic hybrid tandem solar cell with a nanostructured PVSK as the light window and a PFN/doped MoO₃/MoO₃ structure as the interconnecting layer (ICL). In this tandem structure, the PVSK layer is specially designed with a nanostructured surface morphology; thus the PCBM could be filled-up for forming intimately contacted interface with PVSK layers. This design could not only efficiently increase the device performance, it could also greatly remove the hysteresis of PVSK solar cells. The study indicates that doped MoO₃ as the step layer plays a key role in protecting the underlying layer against multi-solution processes and aids in the efficient recombination of electrons and holes generated from the sub-cells. The hybrid tandem solar cell could achieve a high V_{OC} of 1.58 V, which is the sum of those in the two sub-cells, and a high FF of 0.68, indicating the effectiveness of the multilayer ICL.

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Introduction

Photovoltaic technology has been regarded as the most promising way to produce clean energy at an economical cost. Recently, organic-inorganic hybrid perovskite (CH₃NH₃)PbX₃ (X = Cl, Br and I) based solar cells have recently attracted intensive attention due to its high performance, mechanical flexibility and large-area solution-processed fabrication.^{1–6} So far, the continuous efforts have boosted the efficiency of single-junction (SJ) perovskite (PVSK) solar cell over 20%,^{7,8} representing a bright future for their practical application.

The PVSK material is ionic and polycrystalline in nature, which generates Janus effects on its application in thin film solar cells.^{9,10} Firstly, the ionic property endows PVSK with a very high dielectric constant for electrostatic force screening with the charges generated directly after light excitation.¹¹ On the other hand, this property makes PVSK very sensitive to the external environment such as moisture and electrical bias, which brings instability and anomalous hystereses into the devices.^{12–16} In terms of standardization of PVSK solar cells, hysteresis should be eliminated because unstable device performance is undesirable. In addition, hysteresis also hinders

the development of tandem technology, which requires photo-current matching among sub-cells.¹⁷ Exploring the origin of the hysteresis and its solutions is the critical task of future studies. Recently, Shao *et al.* discovered that the hysteresis might originate from the trap states of the PVSK layer and, interestingly, surface n-type PCBM could passivate parts of them with reduced hysteresis.¹⁸ In our recent work, the halide I[−] has been identified as the dominant mobile ion in the PVSK layer, which might result in hysteresis *via* an electrochemical process.¹⁹ Moreover, Xu *et al.* directly incorporated PCBM into the bulk PVSK layer and argued that PCBM could stabilize I[−] with reduced hysteresis.²⁰ Although these strategies, to some extent, resolved the hysteresis problem, there are still some concerns. For example, the PCBM layer atop of the PVSK layer could merely passivate some of the surface traps; while the PVSK-PCBM composite precursor requires an organic solvent to stabilize PCBM molecules, which will reduce the solubility of PVSK and limit the formation of a thick layer for high device efficiency. In this regard, more work should be done to develop efficient strategies for reducing the device hysteresis.

Recently, tandem solar cells using PVSK as the wide band-gap absorber have attracted increasing attention due to their potential for further enhancing device efficiency.²¹ C. Bailie *et al.* first demonstrated a four-terminal tandem architecture cell by integrating a semi-transparent PVSK cell with a transparent Ag nanowires top electrode on top of low band-gap solar cells and achieved improved device performance compared to two single-junction solar cells.²² Similarly, Philipp

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Löper *et al.* reported organic–inorganic halide PVSK/crystalline silicon four-terminal tandem solar cells with an efficiency of 13.4% by using a transparent MoO₃/ITO top electrode.²³ In this four-terminal tandem architecture, the key factor is the transparent top electrode, which is currently still a problem in terms of low cost, high transparency and large conductivity.²⁴ Compared to four-terminal tandem structures, two-terminal tandem architectures, by connecting two sub-cells in series, is much simpler, releasing the need of a transparent top electrode. The advantages of this structure have been proved in the organic bulk heterojunction (BHJ) tandem community with a recorded efficiency of up to 12%.^{25–29} However, two-terminal tandem solar cells based on PVSK have been rarely studied. One possible reason might be that the design of the interconnecting layer (ICL) is difficult. In two-terminal architecture, the ICL serves as the charge-recombination centre and also the protection layer, dominating the final device performance. As is currently known, a PVSK layer is sensitive to aqueous/polar solvents and, in addition, PVSK solar cells usually employ an organic hole-transporting layer (electron-transporting layer) in regular (inverted) architectures to efficiently extract charges and reduce recombination.^{30,31} Therefore, it is very difficult to build an ICL and, subsequently, a second active layer on PVSK sub-cells through a solution process. Considering most of the near-infrared light absorbers, such as organic low-band-gap semiconductors and quantum dots, are processed by organic solvents, this is difficult to accomplish.^{32,33} Smartly, Chen *et al.* recently demonstrated an efficient PVSK/organic BHJ two-terminal tandem solar cell by stacking a PVSK sub-cell on an organic BHJ sub-cell with a water/alcohol processed PFN/TiO₂/PEDOT:PSS ICL.³³ Their study indicates that organic BHJ systems are very promising as spectrally complementary absorbers in two-terminal PVSK tandem architectures and still has large spaces to be developed by molecular design and morphology modification. However, in this PVSK-top architecture, the incident light first comes through the near-infrared organic BHJ sub-cell with parts of short-wavelength photons absorbed by the organic layer, which are expected to be harvested by PVSK sub-cell. The best tandem architecture should manage the photons to be converted by their specialized sub-cells in the most efficient way. In this regard, the proper tandem architecture should use the PVSK layer as the bottom sub-cell and the organic BHJ layer as the rear sub-cell. As mentioned, this tandem structure is difficult to be realized due to the multi-solution processes necessary for construction. For example, the PVSK layer could be destroyed by solution processes with an aqueous PEDOT:PSS layer, even if there is an organic layer such as a PCBM protective layer on it. Hindered by these problems, there are still no reports on PVSK-bottom two-terminal hybrid tandem solar cells despite their importance. The insight of how to optimize the ICL in such a tandem structure is still missing.

In this work, we present PVSK-organic hybrid tandem solar cells with a PVSK sub-cell as the light window and a PFN/Ag (Al)-doped MoO₃/MoO₃ as the interconnection layer. In this tandem structure, the PVSK layer is specially designed with

nanostructured surface morphology; thus the PCBM could be filled-up for forming intimate interface contact with PVSK layers. This design could not only efficiently increase the device performance, but also greatly remove the hysteresis of the planar device. Optical modelling was implemented to guide the design of hybrid tandem solar cells and points out that the dominating factor for the photocurrent in tandem cells is the near-infrared organic sub-cell. The hybrid tandem solar cell could achieve a high V_{OC} of 1.58 V and a FF of 0.68, indicating the effectiveness of the multilayer ICL. Future endeavors for performance enhancement in hybrid tandem solar cells have also been pointed out.

Results and discussion

Single-junction PVSK solar cells

In this work, we use CH₃NH₃PbI_{3–x}Cl_x as the PVSK absorber owing to low-temperature annealing, long charge diffusion lengths and smooth surfaces.^{34,35} As for the device architecture, we chose an inverted planar p–i–n structure by sandwiching the PVSK layer between a p-type PEDOT:PSS and a n-type PCBM layer. The contact between the PVSK layer and the n-type PCBM is supposed to be very important to the device performance. Herein, we adopt the experience from the deposition of sol–gel films from slow-evaporating solutions to shape the surface: when the speed of solvent evaporation is comparable to that of the interaction between solutes, the volume constriction due to the evaporation of solvent molecules will make the film surface shaped.³⁶ As schematically shown in Fig. 1a and b, two types of PVSK layers are prepared by choosing two different recipes. The first PVSK layer is deposited by using low-boiling-point DMF, while the second PVSK layer uses a DMF:DMSO mix with a slow-evaporating speed. Sequentially, both wet films are subjected to low-temperature thermal annealing under vacuum. For the first PVSK layer, the evaporating speed of residual DMF solvent in the film is much faster than the reaction process of the precursor. The obtained film is very smooth and without voids. However, for the second PVSK layer, the evaporating speed of residual DMF:DMSO is comparable with that of the reaction process. Thus, many voids are produced due to volume constriction. The morphologies of the two resultant PVSK films are studied by scanning electron microscopy (SEM) and the corresponding results are shown in Fig. 1c and d. The PVSK layer deposited from DMF is characterized by close-packed crystals with grain sizes of around 200 nm and clear boundaries. On the contrary, the morphology of the PVSK layer from the mixed solvent features uniformly distributed voids with a size of 100 nm and spacing at about 200 nm, and does not show apparent grain boundaries. It should be noted that this nanostructured PVSK film is quite different from the film with incomplete coverage reported previously, which results from the de-wetting process or the over-growth of PVSK crystals, and is supposed to adversely impact device performance.³⁷ For the nanostructured PVSK layer, as shown in Fig. 1e and f, the PCBM can fill up the

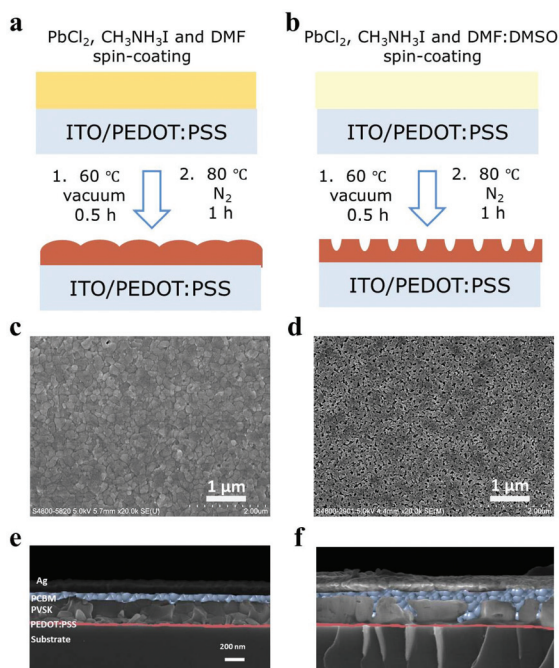


Fig. 1 The schematic formation processes of PVSK films spin-coated from DMF solution (a) and mixed solution (b); SEM images of PVSK films spin-coated from DMF solution (c) and mixed solution (d), and cross-sectional SEM of Substrate/PEDOT:PSS/PVSK layer/PCBM/Ag multilayer based on DMF-processed PVSK (e) and mixed solvent-processed PVSK layer (f).

voids and consequently form a conformable and intimate contact with increased interfacial areas that can contribute to improving the device performance.

Fig. 2 shows the J - V characteristics and corresponding EQE spectra of planar single-junction PVSK solar cells based on the two different recipes. As shown in Fig. 2a, the J - V curve of PVSK solar cells based on boundary-featured film renders severe hysteresis and the corresponding parameters are listed in Table 1. In the forward scanning direction (short circuit to positive bias), the device shows a short-circuit current (J_{SC}) of 18.4 mA cm^{-2} ,² fill factor (FF) of 64.2% and overall PCE of 10.5%. In the reverse direction (positive bias to short circuit), the efficiency of the device was reduced to 7.97% due to the greatly reduced FF and J_{SC} . In stark contrast, the solar cells based on the nanostructured PVSK film exhibit nearly the same device efficiencies (11.9% and 12.2%) in the forward and reverse directions, respectively, as shown in Fig. 2b. Meanwhile, the V_{OC} and FF are greatly enhanced compared to PVSK solar cells prepared from the DMF solution. In previous works, it was suggested that the anomalous hysteresis of PVSK solar cells might arise from ionic migration, charge capture/release by trapped states and electrical polarization.¹⁵ Although the real cause of hysteresis is still under debate, there is evidence that the hysteresis could be reduced by passivating the surface traps with n-type PCBM molecules and reducing the electric field-induced anion migration on boundary sites. For the PVSK

film deposited from the mixed solvent, the PCBM molecules could easily infiltrate the voids, leading to increased interfacial areas between the PVSK film and n-type PCBM molecules. The enhanced interaction between these two layers might enhance the passivation of surface traps and, consequently, reduce the hysteresis. In addition, the grain boundaries, which function as the channel for ion migration, are greatly reduced in the nanostructured film. This might also contribute to reduce the hysteresis. Transient photo-voltage decays in the two types of solar cells are measured to investigate the charge dynamics along the entire pathway in Fig. 2c. The fitted lifetime of photo-generated charges are 1.1 s and 2.1 s for the solar cells prepared from DMF and the mixed solution, respectively. These results indicate that the surface trap states of nanostructured PVSK could be efficiently passivated by PCBM due to the improved contact. Therefore, the trap-assisted recombination channel is shut down and, consequently, the lifetime of photo-generated charges is prolonged. The presence of the voids in the PVSK film processed from the mixed solution would, to some extent, reduce the light extinction capability, but an increased photocurrent is still observed. In Fig. 2d, the external quantum efficiency (EQE) spectra are displayed. The PVSK solar cell prepared from the mixed solvent shows increased photon-electron conversion efficiency with respect to the one from DMF only, which is consistent with the measured photocurrent.

Optimization of interconnecting layer

It is very crucial to choose an appropriate ICL for PVSK-organic hybrid tandem solar cells. The ICL should meet the prerequisites of protecting the underlying layers from the second spin-coating process and realizing energy-loss-free charge recombination. In Fig. 3a, the device architecture with corresponding energy levels for the hybrid tandem solar cell is displayed. The PVSK solar cell is used as the front sub-cell and organic PBDTT-DPP:PC₇₀BM as the rear sub-cell. The ICL employs a trip-layer structure consisting of PFN layer/step layer/MoO₃. The PFN molecules are assembled on the surface of the n-type PCBM layer to form a dipole pointing from the PCBM layer to the step layer, which facilitates the extraction of electrons from the PVSK sub-cell. The high work-function MoO₃ layer is used to form Ohmic contact with the up-lying organic sub-cell for efficient hole extraction. The key part of such a trip-layer structure is the step layer serving as the recombination centre and, simultaneously, as the protection layer. The J - V characteristics of hybrid tandem solar cells with different step layers are demonstrated in Fig. 3b. As pristine MoO₃ film is used as the step layer, the J - V curve of the device shows an apparent S-shaped kink with a low V_{OC} of 1.38 V and a low FF of 0.281. This might result from the big energy level offset between PFN and MoO₃ layers, leading to inefficient charge recombination and electrons (holes) accumulation at each side of the PFN/MoO₃ interface.³⁸ When an Al doped MoO₃ (MoO₃-Al) layer is used as the step layer, the V_{OC} and FF of the hybrid tandem solar cell is greatly improved up to 1.45 V and 0.611 without the S-shape observed in the J - V curve. The MoO₃-Al layer with

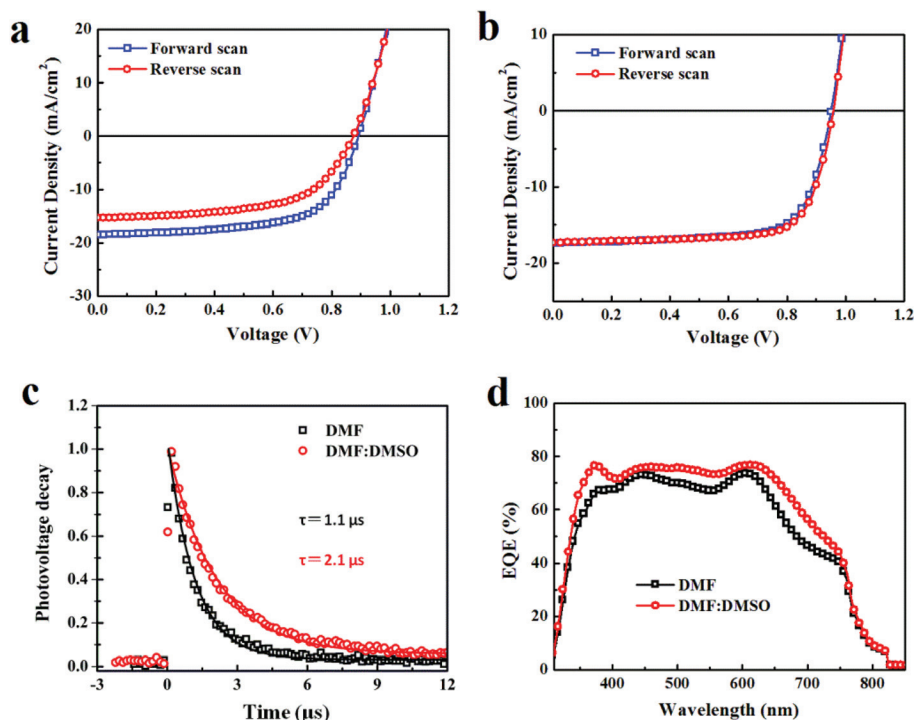


Fig. 2 The J - V characteristics of solar cells based on the boundary-featured PVSK layer (a) and nanostructured PVSK layer (b); The transient photovoltage decay (c) and external quantum spectra (d) of PVSK solar cells.

Table 1 Photovoltaic performance of single-junction PVSK solar cells and hybrid tandem solar cells

Single-junction PVSK solar cells					
Devices	Sweep	V_{OC} [V]	J_{SC} [mA cm ⁻²]	FF	PCE [%]
DMF	Forward	0.89	18.4	0.642	10.5
	Reverse	0.88	15.4	0.588	7.97
DMF : DMSO	Forward	0.95	17.4	0.720	11.9
	Reverse	0.96	17.3	0.733	12.2
Optimization of the ICL					
Step layer		V_{OC} [V]	J_{SC} [mA cm ⁻²]	FF	PCE [%]
MoO ₃		1.38	7.65	0.281	3.26
MoO ₃ -Al		1.45	7.02	0.611	6.17
MoO ₃ -Ag	1.33%	1.37	7.95	0.461	5.02
	6.67%	1.55	8.15	0.535	6.76
	13.3%	1.41	7.65	0.523	5.64
	20.0%	1.41	6.74	0.515	4.89
Optimized hybrid tandem solar cells					
Device		V_{OC} [V]	J_{SC} [mA cm ⁻²]	FF	PCE [%]
Hybrid tandem		1.58	8.02	0.68	8.62
Single-junction PVSK		0.88	10.3	0.73	6.61
Single-junction PBDTT-DPP:PC ₇₀ BM		0.72	14.0	0.63	6.36

a medium WF of 4.5 eV could form cascade energy levels with the PFN and MoO₃ layers, which facilitates the recombination of charge carriers being collected by the PFN and MoO₃ layers.

In addition, it is reported that Al doping could also increase the charge carrier population and, consequently, conductivity of the MoO₃ layer.³⁹ This could not only reduce the bulk resist-

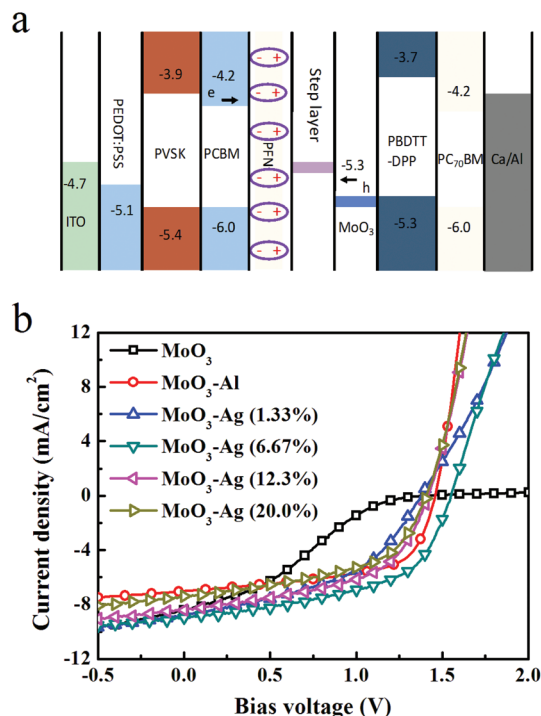


Fig. 3 (a) Device architecture with corresponding energy levels for the hybrid tandem solar cell and (b) J - V characteristics of hybrid tandem solar cells with different ICLs.

ance of the oxide layer, but also decrease the width of the triangle energy barrier at the interface and increase the possibility of tunneling through for charge carriers. The increased charge recombination and reduced resistance are responsible for the enhanced device performance as the MoO₃-Al layer is used as the step layer. To generalize this strategy, stable metallic Ag is further employed to dope the MoO₃ (MoO₃-Ag) layer with varying weight ratios from 1.33% to 20.0%, which are applied as the step layer in hybrid tandem solar cells. The working principle of the ICL is demonstrated in Fig. S1 (ESI†). As the Ag content increases, the WF of the MoO₃-Ag layer is gradually reduced from 5.12 eV to 4.68 eV and the electrons and holes can recombine with reduced resistance and energy losses. The optical transparency of the ICL with different Ag contents is shown in Fig. S2 (ESI†). The transparency of the ICLs decrease quickly when the weight percentage of Ag is over 6.67%. Therefore, the device exhibits the best performance with a V_{OC} of 1.55 V, J_{SC} of 8.15 mA cm⁻², FF of 0.535 and overall PCE of 6.76% when the Ag content is 6.67% with a reduced WF of 4.91 eV for the step layer. The reduced J_{SC} and PCE are observed when the ratio of Ag has high levels due to the decreased optical transparency of the ICL. The metallic atoms also play a role in cross-linking the oxide layer by their interaction with the oxide structure. This makes the film robust and able to withstand the solvent.⁴⁰ This effect also contributes to fabricating efficient hybrid tandem solar cells with reduced energy losses in the ICL.

The optical simulation

It is not a trivial work to optimize hybrid tandem solar cells as each layer is coupled to impact the final device performance. Optical modelling has been evidenced as an effective strategy for guiding the fabrication of multilayer solar cells. Fig. 4 shows the optical simulation of PVSK-organic hybrid tandem solar cells based on the classical transfer matrix method. The optical constants of the PVSK layer and PBDTT-DPP:PC₇₀BM BHJ layer are measured by fitting ellipsometry data and the corresponding results are displayed in Fig. 4a. The PVSK layer exhibits a very strong extinction capability in the short wavelength range of 300 to 600 nm while the organic BHJ layer is a good absorber for long-wavelength photons. The 3D mesh plot of the simulated photo current of the hybrid tandem solar cells versus the thickness combination of the PVSK and PBDTT-DPP:PC₇₀BM layers are shown in Fig. 4b. The internal quantum efficiencies (IQE) of the PVSK sub-cell and the organic sub-cell are assumed to be 100% and 70%, respectively. The maximum photocurrent of hybrid tandem solar cells is usually achieved when the thickness of the organic sub-cell is at its interference peaks (100 nm, 200 nm and 360 nm) while the thickness of the PVSK layer is limited at to the range of 90 to 150 nm. The simulated results indicate that the photocurrent of hybrid tandem solar cells is dominated by that of the organic sub-cells. Given the catastrophic effects of a thick BHJ layer on the performance of organic sub-cells, the optimized hybrid tandem solar cells should keep the thickness of the organic layer at a range of 90–120 nm and the PVSK layer at around 110 nm with an optimized photocurrent of 9.2 to 9.8 mA cm⁻². Fig. 4c shows the 2D contour plot of the opto-electrical field versus the wavelength and position in a hybrid tandem solar cell with a 110 nm thick PVSK layer and a 100 nm thick organic BHJ layer. As can be seen, the short wavelength photons are fully absorbed by the surface of the PVSK layer and hardly penetrate into deeper places. As the wavelength of the photon is increased, the photons gradually penetrate the PVSK layer and contribute to absorption by the organic sub-cell. In the range of 600–800 nm, the maximum value of the opto-electrical field falls upon the middle of the organic BHJ layer. In this regard, the PVSK layer could function as an effective photon filter by allowing the passage of long-wavelength photons and absorbing the short-wavelength photons, which could improve the utilization efficiency of light and, ultimately, boost the device performance.⁴¹ Fig. 4d shows the spatial distribution profile of photo-generated charges in the hybrid tandem solar cells. The generation of charges in the PVSK sub-cell mainly happens at the surface due to the contribution of short wavelength light extinction while the long wavelength photons are converted into charges in the middle of the BHJ layer. Although the electrons in the PVSK sub-cell are required to drift a longer distance than holes generated in the organic sub-cell to reach the ICL for combination, balanced recombination is expected as the charge mobility of the PVSK layer is much higher than that of the organic BHJ layer. This is very distinct from polymer tandem solar cells

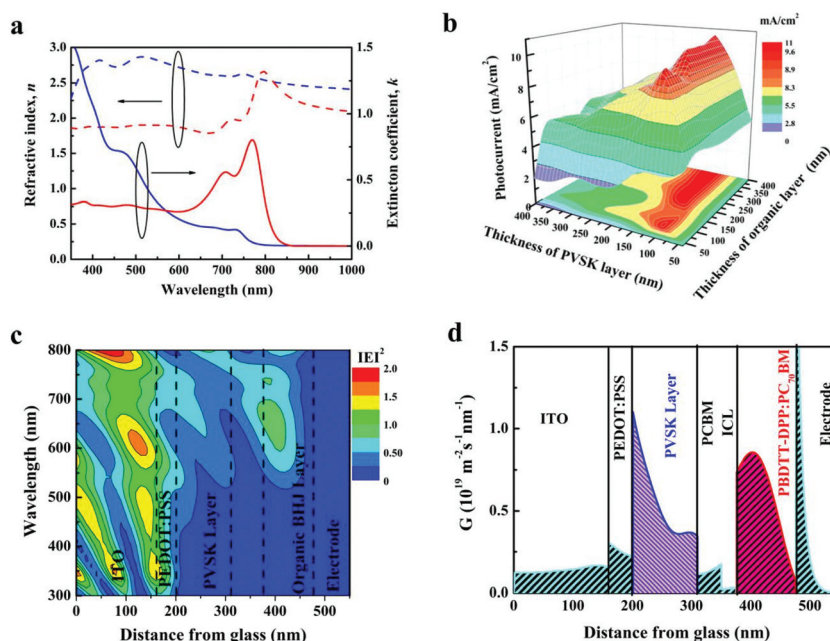


Fig. 4 (a) The optical constants (n and k) of the PVSK layer (blue) and the PBDTT-DPP:PC₇₀BM layer (red). (b) The 3-D mesh plot of simulated photocurrents of hybrid tandem solar cells as a function of the thickness combination of the PVSK layer and the organic BHJ layer. (c) Contour plot of the opto-electrical field profile at different wavelengths. (d) Simulated photocurrent generation in a hybrid tandem solar cell with 110 nm-thick PVSK film and 100 nm-thick organic BHJ layer.

where unbalanced recombination is supposed to adversely impact the device performance with a reduced FF.⁴⁰ In this regard, PVSK-organic hybrid tandem solar cells might be a promising way of converting large-range light into electricity.

PVSK-organic hybrid tandem solar cells

According to the guidelines of the optical modelling, the optimized hybrid tandem solar cells were fabricated with a PVSK

layer thickness and a PBDTT-DPP:PC₇₀BM layer thickness at around 110 nm and 100–120 nm, respectively. The ICL employs the PFN/MoO₃-Ag (6.67%, 15 nm)/MoO₃ (10 nm) multilayer architecture. The J - V characteristics of this hybrid tandem solar cell and the corresponding single-junction reference cells are displayed in Fig. 5a and the corresponding results are listed in Table 1. The best hybrid tandem solar cell achieves a V_{OC} of 1.58 V, a J_{SC} of 8.02 mA cm⁻², a FF of 0.68

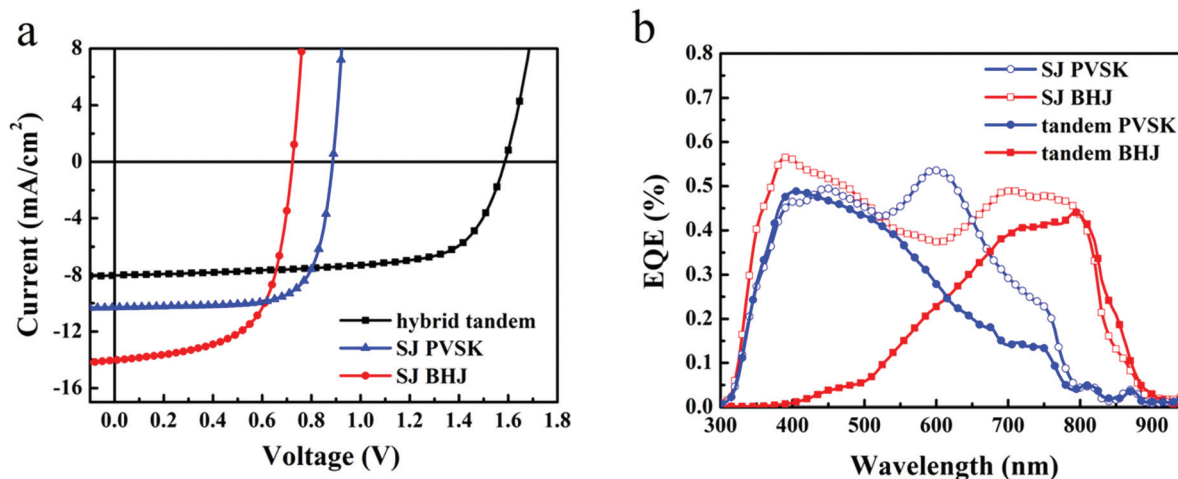


Fig. 5 (a) J - V characteristics of single-junction PVSK and PBDTT-DPP:PC₇₀BM reference solar cells and hybrid tandem solar cell. (b) EQE spectra of two sub-cells in hybrid tandem solar cells and corresponding single-junction reference solar cells.

and an overall PCE of 8.62%, which is higher than those (6.61% and 6.36%) in two sub-cells. The V_{OC} of the hybrid tandem device is the sum of those (0.88 V and 0.72 V) in the two sub-cells, indicating the electrons generated in the PVSK sub-cell could efficiently recombine with the holes from the organic sub-cell with ignorable energy loss. The relatively high FF value implies small resistance from the ICL and the absence of charge accumulation at the ICL due to efficient charge recombination. External quantum efficiency (EQE) spectra of the corresponding solar cells are demonstrated in Fig. 5b. The PVSK and organic BHJ sub-cells, which convert short-wavelength and long-wavelength light, respectively, achieve a matched photocurrent. It is noted that the J_{SC} of the hybrid tandem solar cell is only 8.02 mA cm^{-2} , which is lower than the predicted value of 9.3 mA cm^{-2} from optical modelling. This discrepancy mainly results from the less efficient organic sub-cell than the assumed value in optical modelling. The photocurrent of the hybrid tandem solar cell is dominated by the photocurrent generated from the organic infrared sub-cell. It is envisioned that the advanced design of organic infrared materials by increasing the mobility for efficient photon-electron conversion, and reducing the spectral overlap with PVSK, could push the device performance of such hybrid tandem solar cells up to an encouraging level.

Conclusions

In this work, we report a PVSK-organic hybrid tandem solar cell based on a nanostructured PVSK layer as the light window and a PFN/doped- $\text{MoO}_3/\text{MoO}_3$ multilayer ICL. Nanostructured engineering of the PVSK layer has been proved to be an effective strategy for enhancing the electronic coupling between the PVSK layer and the n-type PCBM, which helps to reduce trap states and eliminate device hysteresis. Optical modelling was used to guide the fabrication of such hybrid tandem solar cells. The simulation results indicated that the PVSK layer could function as an effective filter for converting short-wavelength photons while allowing long-wavelength photons to pass and be used by the near-infrared sub-cell. The best hybrid tandem solar cell achieves a V_{OC} of 1.58 V, which is the sum of those in the two sub-cells, and a high FF of 0.68. This indicates the effectiveness of the ICL in allowing the charges to recombine without energy loss. It is expected that the development of advanced organic infrared photoactive materials will push the efficiency of such hybrid tandem solar cells up to a higher level.

Experimental section

Materials

PBDTT-DPP polymer & PFN, PCBM and PC_{70}BM were purchased from 1-Material Inc., Solarmer Materials Inc. and Nano-C, respectively. $\text{CH}_3\text{NH}_3\text{I}$ was synthesized by following the reported procedure.⁴ PbCl_2 (Aldrich) and $\text{CH}_3\text{NH}_3\text{I}$

were mixed in DMF or the DMF/DMSO (0.8:0.2 in Volume) solution at a molar ratio of 1:3 with different weight percentages.

Single-junction device fabrication

ITO coated glass slides were cleaned by ultra-sonication for 30 minutes in detergent water, de-ionized water, acetone and ethanol, sequentially. The ITO substrates were then subjected to UVO treatment for 25 minutes. The PEDOT:PSS layer were spin-coated onto the ITO substrates. For the single-junction planar PVSK solar cells, the precursor in mixed DMF/DMSO solvent (60 wt%) was spin-coated onto the PEDOT:PSS layer. As a reference, the precursor in DMF solvent (60 wt%) was also spin-coated onto a PEDOT:PSS layer. The obtained films were subjected to low-temperature (60 °C) annealing under vacuum for 40 minutes in order to remove the solvent. Then, the sequential films were annealed at 80 °C for one hour to transfer the PVSK layers with a thickness of 220 nm. Then, the 40 nm thick PCBM layer was deposited onto the PVSK layer as a n-type layer and a PFN film with a thickness of 1 nm was spin-coated as an interfacial layer. Finally, a 80 nm thick Ag was thermally deposited as the cathode. For single-junction organic solar cells, the PBDTT-DPP/ PC_{70}BM blended solution (1:2, 18 mg ml^{-1} in 1,2-dichlorobenzene *o*-DCB) was spin-coated onto the PEDOT:PSS layer to form a 110 nm thick layer. Ca (20 nm)/Al (100 nm) were sequentially thermal-evaporated as the cathode. The area of the cells was 0.06 cm^2 as defined by the mask.

Tandem device fabrication

The fabrication of the front sub-cell mainly followed the procedure for the preparation of the single-junction device until the Ag cathode was deposited. The only difference was the variation of the PVSK layer thickness for optimization of the tandem devices. Sequentially, the Ag or Al doped $\text{MoO}_3/\text{MoO}_3$ bi-layer was deposited as an ICL, where the co-evaporation technique was used for the doped- MoO_3 layer deposition. The content of Al in MoO_3 -Al step layer was kept between 40 and 50 wt%. The PBDTT-DPP/ PC_{70}BM blended solution (1:2, 18 mg ml^{-1} in 1,2-dichlorobenzene *o*-DCB) was spin-coated onto the PEDOT:PSS layer to form a 110 nm thick layer. Ca (20 nm)/Al (100 nm) were sequentially thermal-evaporated as the cathode. The area of the cells was 0.06 cm^2 as defined by the mask.

Device characterization

The work functions of different layers were measured by a Kelvin probe. The morphology of the PVSK layers on ITO/PEDOT:PSS substrates were characterized by scanning electron microscopy (SEM, Hitachi S-4800). The refractive index (n and k values) of the layers in the device structure was measured using a VASE ellipsometer from J. A. Woollam Co., Inc. Current density-voltage (J - V) characteristics were obtained by using a Keithley 2635 source meter and Newport AM 1.5G solar simulator with irradiation intensity of 100 mW cm^{-2} . The

thicknesses of the layers were measured by a Dekak Stylus Profiler.

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