



The fabrication of homogeneous perovskite films on non-wetting interfaces enabled by physical modification

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ABSTRACT

Conjugated polymers are commonly used as effective hole transport materials (HTMs) for preparation of high-performance perovskite solar cells. However, the hydrophobic nature of these materials renders it difficult to deposit photovoltaic perovskite layers on top via solution processing. In this article, we report a generic surface modification strategy that enables the deposition of uniform and dense perovskite films on top of non-wetting interfaces. In contrast to the previous proposed chemical modifications which might alter the optoelectronic properties of the interfacial layers, we realized a nondestructive surface modification enabled by introducing a layer of insulating mesoporous aluminum oxide (Al_2O_3). The surface energies of the typical non-wetting hole-transport layers (PTAA, P3HT, and Poly-TPD) were significantly reduced by the Al_2O_3 modification. Benefiting from the intact optoelectronic properties of the HTMs, perovskite solar cells deposited on these interface materials show full open-circuit voltages (V_{oc}) with high fill factors (FF) up to 80%. Our method provides an effective avenue for exploiting the full potential of the existing as well as newly developed non-wetting interface materials for the fabrication of high-performance inverted perovskite solar cells.

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1. Introduction

Organic-inorganic halide perovskite solar cells (PSCs) have attracted substantial attention as a next-generation photovoltaic technology due to their simple device architecture, low fabrication cost and outstanding photovoltaic performance [1–4]. In the past decade, the power conversion efficiency (PCE) of PSCs has increased from 3.8% to over 23% [3,5–9]. The impressive enhancement in efficiency of PSCs is mainly related to the rapid development of solution processing strategies, which enables the deposition of high-quality perovskite absorbers on various charge-collecting materials [10–12]. Typically, perovskite solar cells can be constructed in either a normal structure (n-i-p) or an inverted (p-i-n) structure, depending on the position of the hole and electron transport layers in the device [13]. Normal architecture devices

using mesoporous or planar metal oxides as electron-collecting layers, such as titanium oxide, zinc oxide, tin oxide, have realized high efficiencies, which, however, brought about stability issues due to the presence of few dopants in the hole transport layers [14,15]. Moreover, the high-temperature sintering step involved in the fabrication of metal oxide layers represents a major hindrance for low-temperature manufacture of PSCs on flexible substrates.

Alternatively, inverted structure PSCs using undoped hole transport materials have received growing interest due to their low-temperature processing and easy fabrication [16,17]. Moreover, the inverted device configuration possesses several appealing features, including negligible hysteresis, compatibility with high-throughput roll-to-roll processing, and has demonstrated high PCEs comparable to those of normal structure devices [16]. In inverted PSCs, the choice of hole transport materials plays a crucial role in determining the photovoltaic performance as well as stability of the devices. Owing to its good conductivity, high transparency and excellent film formation, the hydrophilic poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS) has been widely used as HTMs for constructing

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inverted PSCs [18–21]. However, the devices suffered from low V_{OC} due to the energetic mismatch between the work function of PEDOT:PSS (–4.9 to 5.1 eV) and valence band of perovskites (around 5.5 eV) [19–21]. In addition, the corrosive and hygroscopic nature of PEDOT:PSS can have detrimental effect on the long-term stability of the solar cells.

Alternatively, hydrophobic HTMs with better energy level alignment with perovskites hold the great potential in delivering high V_{OC} and, thus, overall high device performance. However, the non-wetting properties of these conjugated polymers such as poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) [10,22,23], Poly[N,N'-bis(4-butylphenyl)-N,N'-bis(phenyl)benzidine] (Poly-TPD) [10,24,25], poly(3-hexylthiophene-2,5-diyl) (P3HT) [26] make it difficult to deposit photoactive perovskite layer on top via solution processing, which represents a major bottleneck limiting the development of low-temperature solution processed inverted PSCs. To address this dilemma, surface modifications via oxygen plasma or ultraviolet-ozone (UVO) treatment have been employed to decrease the surface energy of the hole transport layers (HTLs) [26,27]. For example, Xu et al. recently reported the surface modification of hydrophobic hole transport material Poly-TPD by means of UVO treatment [27]. Similarly, Zhang and co-authors demonstrated the use of oxygen plasma to decrease the surface energy of non-wetting hole transport materials [26]. Despite the effectiveness of the strategies in reducing the surface energy, these plasma-based surface modifications can negatively change the chemical structure of the surface and, thus, alter the optoelectronic properties of the HTLs, such as work function, transparency and even mobility of the films [27]. Moreover, the sensitivity to the processing parameters, such as the power of the plasma and processing time, imposes repeatability concerns of the device fabrication [27]. In this context, the development of a non-destructive surface modification method to facilitate the fabrication of high-quality perovskite films on a variety of non-wetting HTLs is highly demanded.

In this article, we report a simple yet effective method that allows the deposition of homogeneous photovoltaic perovskite layer on various non-wetting HTLs. As a decisive step, we ingeniously deposited a mesoporous insulating Al_2O_3 as a physical surface modifier that enables the modulation of the wettability of the perovskite solutions on the non-wetting HTLs. A distinct advantage of our strategy over the previous approaches is that the insertion of the mesoporous insulating Al_2O_3 layer does not deteriorate the chemical properties of the HTLs surface, thus allowing the preservation of the original optoelectronic properties of the HTLs. The success and general application of the strategy was demonstrated by the deposition of uniform and dense perovskite films on three typical hydrophobic HTMs of PTAA, Poly-TPD and P3HT. Inverted planar perovskite solar cells achieved moderate efficiency of 17.41% with FFs approaching 80% and high V_{OC} of up to 1.09 V.

2. Experimental

2.1. Materials

Lead iodide (PbI_2 , 99.9985% metals basis) and cesium iodide (CsI, 99.99% metals basis) were purchased from Alfa Aesar. Lead bromide ($PbBr_2$, 99.999% trace metals basis) and aluminum oxide nanoparticles (Al_2O_3 , <50 nm particle size, 20 wt% in isopropanol) were purchased from Sigma-Aldrich. Methylammonium bromide (MABr), formamidinium Hydroiodide (FAI), bathocuproine (BCP), and PTAA were purchased from Xi'an Polymer Light Technol. Corp. Poly-TPD, P3HT, [6,6]-phenyl- C_{61} -butyric acid methyl ester (PCBM) were purchased from Lumtec. Organic solvents including anhydrous N,N-dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), chlorobenzene (CB), ethyl acetate (EA) and isopropanol were

purchased from Sigma-Aldrich. All commercial materials were used as received.

2.2. Preparation of perovskite solution

Triple-cation mixed halide perovskite precursor solution with the formula of $Cs_{0.05}(FA_{0.82}MA_{0.14})_{0.95}Pb(I_{0.85}Br_{0.15})_3$ was prepared according to the reference with some modifications [28]. Specifically, a 1.5 M of $FAPbI_3$ (FAI, 234.7 mg; PbI_2 , 691.5 mg) and a 1.5 M of $MAPbBr_3$ (MABr, 152.84 mg; $PbBr_2$, 550.5 mg) dissolved in 4:1 V:V dimethylformamide (DMF)/dimethyl sulfoxide (DMSO) were first prepared. The two precursor solutions were placed on a hot plate and heated to 60 °C until the powder dissolved completely. The final perovskite solution was prepared by mixing the $FAPbI_3$ and $MAPbBr_3$ precursor solutions in a 6:1 volume ratio and then adding 35 μ L of CsI stock solution (390 mg in 1 mL DMSO). The perovskite solution stirred more than 2 h before use. It is noted that the lead is 9% mole ratio excess in the triple-cation perovskite system.

2.3. Solar cell fabrication

ITO glass substrates were sequentially cleaned with 2% Hellmanex solution, deionized water, anhydrous ethanol, acetone and isopropanol in an ultrasonic bath for 10 min each, followed by plasma cleaner treatment for 10 min. The interface PTAA (1.5 mg mL^{-1} in CB), Poly-TPD (1.5 mg mL^{-1} in CB) and P3HT (2 mg mL^{-1} in CB) solutions were spin-coated on the ITO surface at 6000 rpm for 30 s with 3 s acceleration time. The prepared interface layers were annealed at 100 °C for 10 min to drying the solvent. Afterwards, Al_2O_3 nanoparticles with desired concentrations (1:10, 1:25, 1:50, 1:75, 1:100 V:V diluted in isopropanol) were spin-coated on top of the interface layers. Prior to deposition of perovskite layer, the entire stack was annealed at 120 °C for 20 min in air. To prepare the perovskite absorber layer, the substrates were taken into the N_2 -filled glovebox. 80 μ L perovskite solution was dropped on top of the interface layers and spin-coated at 6000 rpm for 30 s with an acceleration rate of 2000 rpm/s for 3 s. 10 s before the end of the spin coating, 200 μ L of ethyl acetate was dropped to the rotating perovskite precursor film. Subsequently, the entire substrate was annealed on a hot plate at 100 °C for 30 min. Having deposited the perovskite layer, 70 μ L PCBM (15 mg mL^{-1} in CB) and 90 μ L BCP (saturated solution in isopropanol) were sequentially spin-coated at 2000 rpm for 30 s and at 4000 rpm for 30 s, respectively. To complete the device, 120 nm thick Ag was thermally deposited. The active area of the solar cells is 9 mm^2 which is defined by overlapping of the bottom ITO and top Ag electrodes.

2.4. Characterization

Optical absorption measurements were performed on an Agilent Cary 5000 spectrophotometer. Morphologies of the Al_2O_3 nanoparticles and perovskite films were imaged with a scanning electron microscope (SEM, FEI Apreo LoVac). The structural property of the perovskite films was analyzed by a Bruker D8 Advance X-ray diffractometer (XRD) using $Cu K\alpha$ as the radiation source. The water contact angles of HTMs were measured by a Micro Capture Pro coupled with Image J software. The transient photovoltage decay characteristics were measured using an electrochemical workstation (ZAHNER, Germany). The current density–voltage (J–V) characteristics and steady-state output of the all solar cells were measured using a Keithley 2400 source meter. The illumination was provided by a Newport Oriel 92,192 solar simulator with an AM1.5 G filter, operating at 100 $mW cm^{-2}$, which was calibrated by a standard silicon solar cell from Newport.

3. Results and discussion

It is known that the surface energy of the interface layers plays a crucial role in determining the solution processability and crystal morphology of the perovskite thin films. Hydrophobic interfaces have been demonstrated to be beneficial for growing perovskite films with large crystal grains [10]. However, the notable difference between the surface energies of the hydrophobic interfaces and the hydrophilic perovskite precursor solutions can result in incomplete surface coverage of the photoactive perovskite films with numbers of pinholes. In some circumstances, de-wetting was frequently observed due to the superior hydrophobic properties of the interface layers, which prohibits the applicability of those promising interface materials that are non-wetting to perovskite precursor solutions.

In 2012, Snaith's group proposed a "meso-superstructured" perovskite solar cell where a layer of mesoporous Al_2O_3 nanoparticle functioning as an inert scaffold was deposited on top of the electron transport layer [29]. Significantly, it is found that the presence of the Al_2O_3 nanoparticle does not deteriorate the device performance. Inspired by this observation, in the present work, we endeavor to achieve the goal of surface energy modifications of non-wetting hole transport materials via insertion of a layer of insulating nanoparticles. We chose Al_2O_3 nanoparticle as the surface modifier based on the following three considerations. Firstly, Al_2O_3 nanoparticles are dispersed in alcohol-based solvent, which can be easily deposited on top of the hydrophobic films. Secondly, the wide bandgap of the Al_2O_3 (7 to 9 eV) will not sacrifice the transparency of the interface layers [29,30], so that it does not contribute to the parasitic absorption losses. Lastly, the hydrophilic properties of the Al_2O_3 can facilitate the spread of perovskite precursor on the hydrophobic interfaces, thus, enabling preparation of uniform perovskite films over large areas.

To illustrate the general applications of the proposed physical surface modification method, we choose three conjugated semiconductors (PTAA, Poly-TPD and P3HT) as representative non-wetting HTMs for construction of perovskite solar cells. Fig. 1 shows the chemical structures of the three HTMs. The presence

of alkyl side chains imparts hydrophobic nature of the three materials in their solid film. As indicated in Fig. S1, the PTAA and Poly-TPD coated on ITO substrates show high transmittances in the visible range, while the slightly low transmittance of P3HT at below 650 nm can be ascribed to its low bandgap of 1.9 eV [31]. The high transparency of the three HTMs renders them as ideal candidates for construction of perovskite solar cells. As shown in Fig. S2, without surface modification, perovskite films can be hardly deposited on top of the three polymers. Particularly for Poly-TPD and P3HT, the perovskite precursor solutions were completely swept from the substrate during spin-coating. In distinct contrast, upon pre-coating a layer of mesoporous Al_2O_3 nanoparticles on top of the three non-wetting interfaces, uniform perovskite films with excellent surface coverage was obtained. To investigate the impact of Al_2O_3 nanoparticles on the wettability of the hydrophobic interfaces, we evaluated the surface energies of the films upon Al_2O_3 treatment by means of water contact angle measurements. The surface modification was achieved by depositing a layer of Al_2O_3 nanoparticles from 50 times diluted suspensions on top the three HTLs. As displayed in Fig. 1, it is obvious that the hydrophobic nature of the as-deposited PTAA, Poly-TPD and P3HT films was demonstrated by the large contact angle of 95.1°, 98.2° and 104.3°, respectively. Significantly, upon the deposition of a layer of Al_2O_3 nanoparticles, the surface energies of the three films were largely decreased, translating to hydrophilic surfaces with contact angles of < 90°.

The low surface energy of the Al_2O_3 modified interfaces enables the facile deposition of perovskite film via one-step solution processing which, otherwise, would not be easily realized without the treatment. To examine the quality of the perovskite films deposited on top of the three Al_2O_3 modified hydrophobic HTLs, we scrutinized the morphology of the perovskites by performing SEM imaging. The SEM images in Fig. 2(a) indicate that all the three polycrystalline perovskite films show similar crystal size of 200–400 nm and exhibit complete surface coverage. The similar grain sizes and morphologies indeed validate the effectiveness of the surface modification, despite of the noticeable difference in surface energies of the unmodified HTLs. We further investigated the crystal structure of the perovskite films using XRD, and the result is shown in Fig. 2(d). It is found that the three perovskites have similar crystal structure, where the characteristic peaks at 14.1°, 20.0°, 24.6°, 28.4° and 31.8° are indexed to the (110), (200), (202), (220) and (310) planes, respectively. In addition, a small diffraction peak at 12.7° was observed which can be ascribed to the (001) plane of the cubic PbI_2 . The intentionally introduced small amount of excess PbI_2 was reported to be beneficial for device performance due to the surface passivation [32–34].

It should be highlighted that the successful implementation of surface modification was realized by introducing a layer of alumina nanoparticles on top the hydrophobic interfaces. We further note that the above-mentioned Al_2O_3 nanoparticles were deposited from 50 times diluted suspensions, which shows an incomplete surface coverage (Fig. 3c). We therefore continue to investigate the impact of the Al_2O_3 coverage on the surface energies of the HTLs and the crystal morphologies of perovskites deposited on top. Fig. 3 (top row) shows the SEM images of the Al_2O_3 nanoparticles with different concentrations deposited on top of ITO/PTAA. It is found that higher concentrations of Al_2O_3 can result in higher surface coverage, while 1:10 diluted suspension leads to a complete surface coverage and possesses a mesoporous structure which is analogous to that of mesoporous n-type metal oxide in normal structure PSCs [29,35]. Significantly, we observed that the surface energies of the interfaces were closely linked to the Al_2O_3 surface coverage. As indicated in the Fig. 3(f–j), for the Al_2O_3 with incomplete coverage, the contact angle gradually decreased from 89.7° to 64.8° for the 1:100 to 1:25 diluted

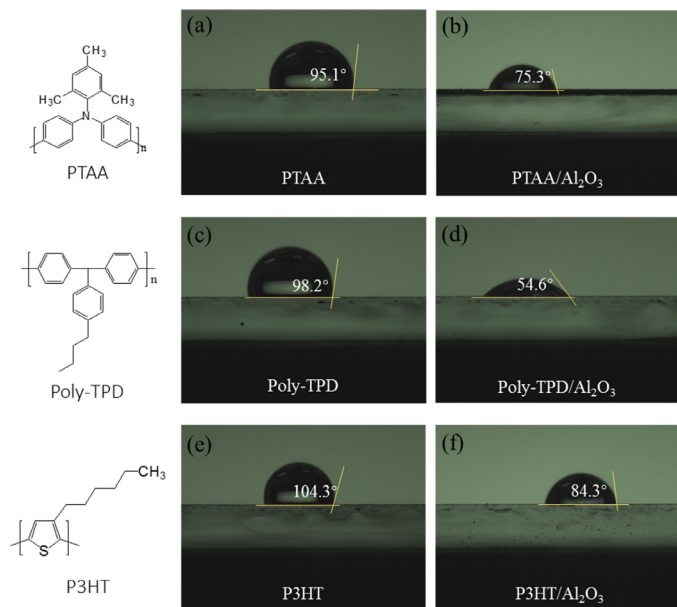


Fig. 1. Chemical structure of the investigated hole transport films and the corresponding water contact angles: the as-deposited (a) PTAA, (c) Poly-TPD, and (e) P3HT, and the respective surface modified with Al_2O_3 (b) PTAA, (d) Poly-TPD, and (f) P3HT.

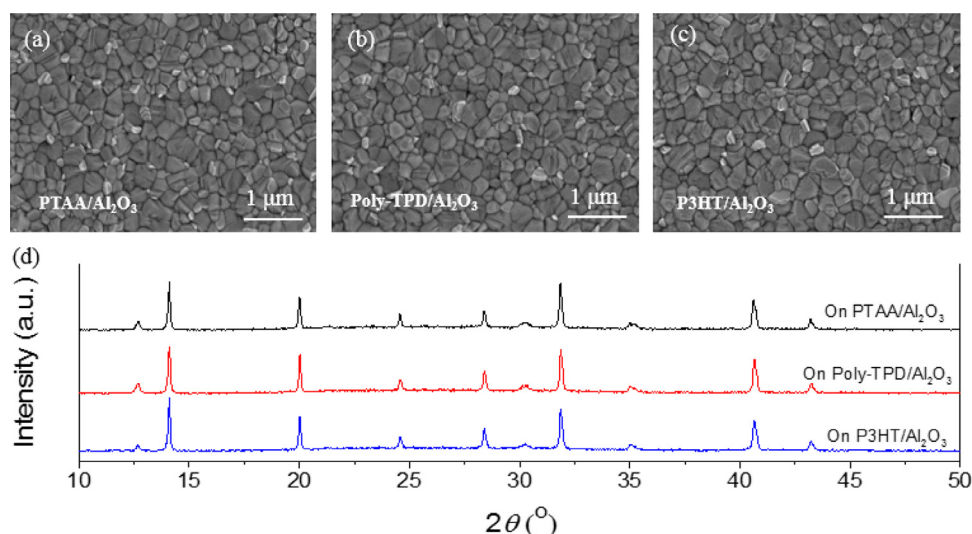


Fig. 2. SEM images of the perovskite films deposited on the three Al_2O_3 -modified hole transport films: (a) PTAA/ Al_2O_3 , (b) Poly-TPD/ Al_2O_3 , and (c) P3HT/ Al_2O_3 , and the corresponding XRD spectra (d).

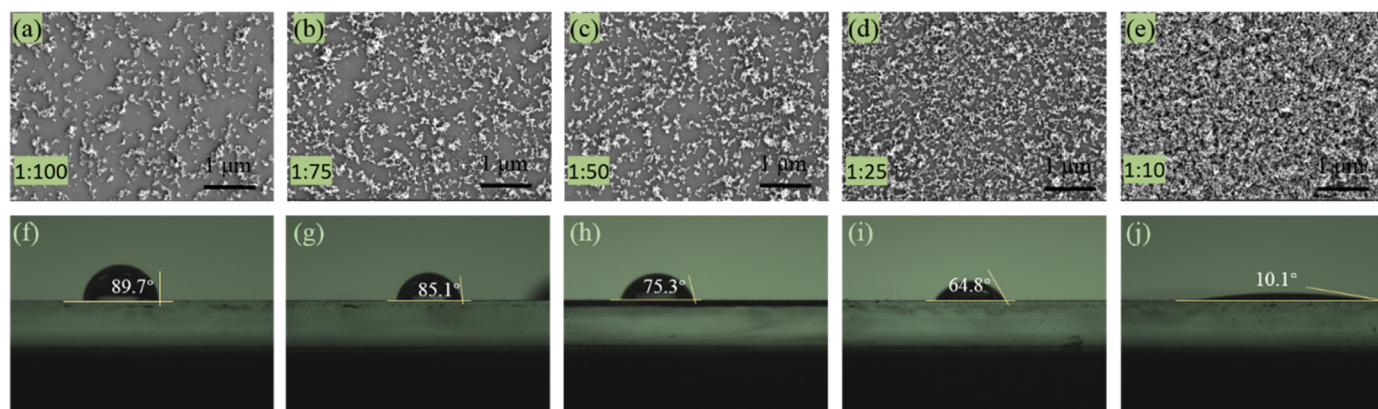


Fig. 3. Top-view SEM images of the Al_2O_3 nanoparticles with different concentrations deposited on ITO/PTAA (diluted with different volume ratios of isopropanol): (a) 1:100, (b) 1:75, (c) 1:50, (d) 1:25, and (e) 1:10. (f)–(j) are the corresponding water contact angles of the surface shown in (a)–(e).

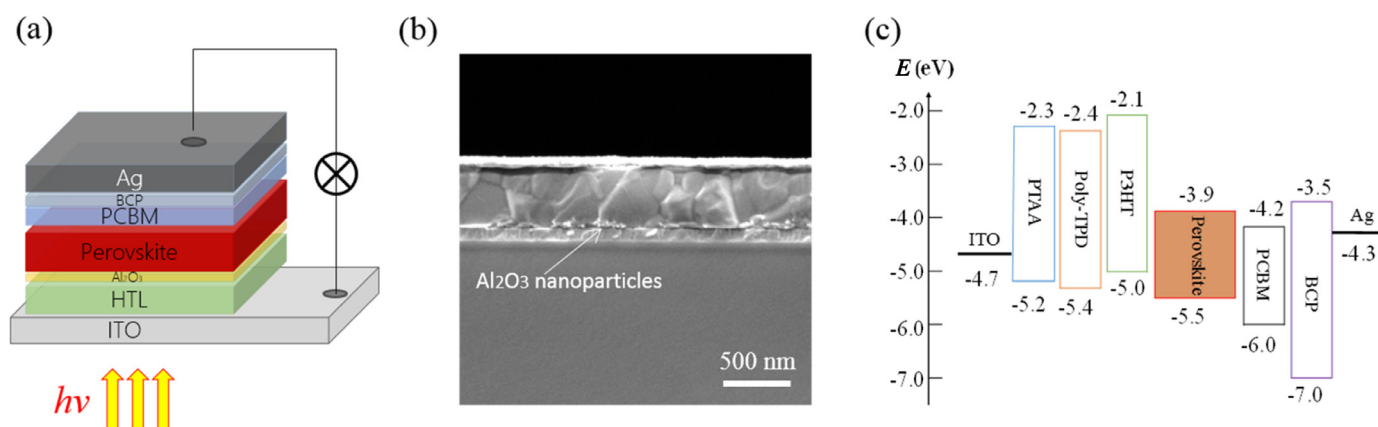


Fig. 4. (a) Device architecture. (b) Cross-sectional SEM image of a complete solar cell stack. (c) Schematic energy level diagrams of the non-wetting HTMs based inverted perovskite devices.

suspensions. When the Al_2O_3 was 10 times diluted, the contact angle was drastically decreased to 10.1° (Fig. S3). The dependence of the contact angle on the surface coverage of Al_2O_3 nanoparticles can be ascribed to the increase in the surface area due to the formation of nanopores and hydrophilic property of the Al_2O_3

nanoparticles [36]. We are curious to examine the morphology of the perovskite films deposited on these interfaces with different hydrophilic properties. To our surprise, the SEM images shown in Fig. S4 evidences that the prepared perovskite films exhibited rather similar morphologies in terms of grain size, surface

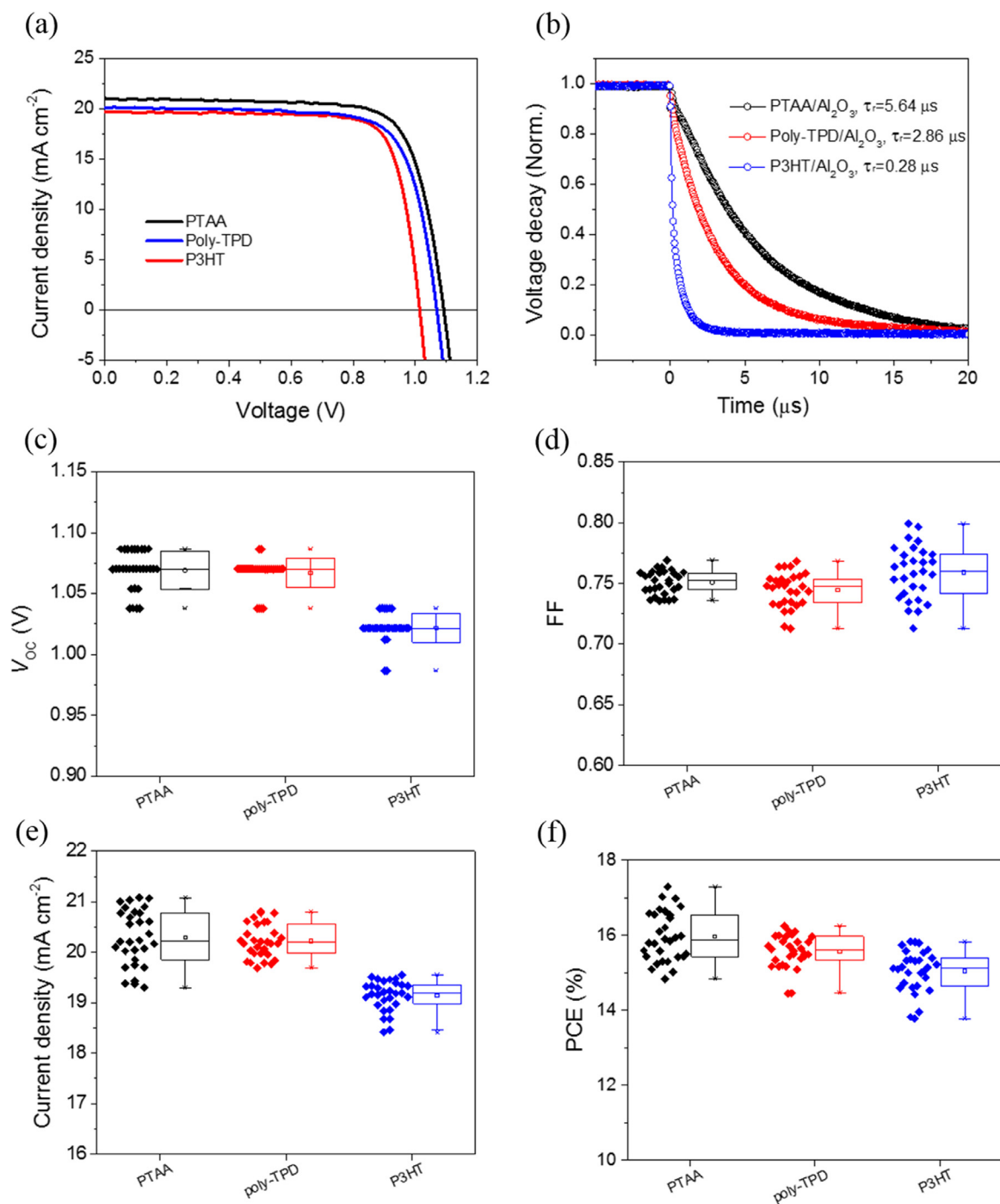


Fig. 5. (a) J-V characteristics of the best-performing perovskite solar cells with Al_2O_3 modified PTAA, Poly-TPD, and P3HT hole transport layers. (b) The corresponding normalized transient photovoltage (TPV) of the three solar cells. (c)–(f) The statistic photovoltaic parameters of the three solar cells: V_{oc} (c), FF (d), J_{sc} (e), and PCE (f).

coverage, which is independent of the surface energies of the HTLs beneath. The XRD spectra confirm that the resulting perovskite films possess similar crystal structure and crystallinity (Fig. S5).

To study the effectiveness of the surface modification of the hydrophobic interfaces as HTL for photovoltaic applications, inverted planar perovskite solar cells with a device structure of “ITO/HTL/ Al_2O_3 /perovskite/PCBM/BCP/Ag” were constructed (Fig. 4a). The cross-sectional SEM image of a typical solar cell is presented in Fig. 4(b), where the surface modifier Al_2O_3 nanoparticles with a non-continuous coverage can be clearly seen in the device stack. Fig. 4(c) illustrates the energy level alignment of the three HTM within the solar cell stack. The energy levels of the

interface materials were taken from the references [12,15,37,38]. It is seen that the Poly-TPD and PTAA exhibit the highest occupied molecular orbitals (HOMOs) of -5.4 and -5.2 eV, respectively, which are more closer to the valence band of the perovskite than that of P3HT. The matched energy level alignment can be expected to deliver high V_{oc} values by providing efficient charge transfer from perovskite to the HTLs and increased quasi-Fermi-level splitting [39].

Fig. 5(a) shows the photocurrent density-voltage (J-V) characteristics of the best-performing perovskite solar cells deposited on Al_2O_3 modified non-wetting HTMs of PTAA, poly-TPD and P3HT. The devices were measured under simulated air mass

Table 1. Photovoltaic parameters of the best-performing perovskite solar cells deposited on the three non-wetting HTMs.

HTM	HOMO (eV)	J_{SC} (mA/cm ²)	V_{OC} (V)	FF (%)	PCE (%)
PTAA	5.2	21.08	1.09	76	17.46
Poly-TPD	5.4	20.08	1.07	75	16.11
P3HT	5.0	19.73	1.02	79	15.90

1.5 G spectrum with intensity of 100 mW cm⁻² in a forward scanning direction. The corresponding photovoltaic parameters of the three solar cells are summarized in Table 1 with the statistic parameters presented in Fig. 5(c–f). The J–V curves indicate that the PTAA-based device yields the highest power conversion efficiency (PCE) of 17.46% with short-circuit density (J_{SC}) of 21.08 mA cm⁻², open-circuit voltage of 1.09 V, and fill factor of 76%. Significantly, all the three devices show negligible hysteresis (Fig. S6), suggesting efficient electron and hole extraction in the devices without accumulation at the interfaces [40,41]. However, it is noticeable that the solar cells deposited on PTAA and Poly-TPD HTMs exhibit V_{OC} values of up to 1.09 V, which is ~0.5 V higher than that of P3HT based device. The obtained high V_{OC} can be due to the favorable energy alignment between the HOMO levels of the PTAA and Poly-TPD and the valence band of perovskite (Fig. 3c), which facilitates the efficient charge transport at the interfaces without significant recombination.

To further unveil the origin of the V_{OC} difference of the devices, we measured the transient photovoltage (TPV) characteristic of the solar cells operated at open circuit conditions, and the results are shown in Fig. 5(b). The charge recombination time (τ_r) is extracted as the time interval during which the photovoltage decays to 1/e of the its initial value immediately after decay [42]. It is found that the PTAA based perovskite device exhibits a highest carrier decay time of 5.64 μ s, which is approximately twofold and 20 times higher than that of Poly-TPD (τ_r = 2.86 μ s) and PH3T (τ_r = 0.28 μ s) based solar cells, respectively. The longer carrier decay time indicates slower charge recombination at the interfaces, which should be the main factor responsible for the enhanced V_{OC} of the PTAA and Poly-TPD based perovskite solar devices.

Finally, to investigate the robustness of the Al₂O₃-based physical modification strategy, we fabricated and evaluated the device performance of PTAA-based PSCs with different Al₂O₃ surface coverages. The statistic device performance is presented in Fig. S7. We can see that thin Al₂O₃ layers (1:100 and 1:75 diluted) result in lower FF and V_{OC} , which can be ascribed to lower quality of perovskite films crystallized on the inferior wetting properties of the HTMs, while the thick Al₂O₃ nanoparticles (1:10 diluted) can impede the hole transport toward the interfaces due to the insulating properties of the Al₂O₃. Consequently, the low J_{SC} values were obtained. Nevertheless, these results demonstrate that depositing a layer of Al₂O₃ nanoparticles can be an efficient nonconstructive surface modification method provided a proper layer thickness is chosen. We have also compared the photovoltaic performance of the solar cells with perovskite absorber layer deposited on Al₂O₃-modified PTAA and plasma-treated PTAA films. As presented in Fig. S8, the plasma treated PTAA films show lower V_{OC} values which can be due to the change of work-function that leads to the energy level mismatch between the PTAA and perovskite films. This observation illustrates the advantage of our Al₂O₃-based physical modification strategy for the preparation of high-performance perovskite solar cells.

4. Conclusions

In summary, we have developed a simple yet effective surface modification strategy that enables the deposit high-quality perovskite films on top of non-wetting surfaces. Central to this

strategy is the introduction of a layer of mesoporous Al₂O₃ as a physical surface modifier, which can efficiently decrease the surface energy of the hydrophobic HTMs. Significantly, it is found that the presence of the insulating non-continuous Al₂O₃ layer does not disturb the transport of holes from the photoactive layer to the HTLs. Planar p–i–n solar cells with typical non-wetting HTMs showing moderate efficiency of up to 17.46% with fill factors up to 80%. Significantly, the obtained full V_{OC} for the respective devices demonstrated the advantages of the proposed Al₂O₃-based physical modifications. Our method opens a practical avenue for the application of the existing and novel non-wetting HTMs for the manufacture of efficient inverted PSCs.

Conflict of interest

The authors declare no competing financial interest.

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Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jechem.2019.03.033.

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