Enhancing the efficiency of planar heterojunction perovskite solar cells via interfacial engineering with 3-aminopropyl trimethoxy silane hydrolysate

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The interfacial compatibility between compact TiO₂ and perovskite layers is critical for the performance of planar heterojunction perovskite solar cells (PSCs). A compact TiO₂ film employed as an electron-transport layer (ETL) was modified using 3-aminopropyl trimethoxy silane (APMS) hydrolysate. The power conversion efficiency (PCE) of PSCs composed of an APMS-hydrolysate-modified TiO₂ layer increased from 13.45 to 15.79%, which was associated with a significant enhancement in the fill factor (FF) from 62.23 to 68.04%. The results indicate that APMS hydrolysate can enhance the wettability of γ-butyrolactone (GBL) on the TiO₂ surface, form a perfect CH₃NH₃PbI₃ film, and increase the recombination resistance at the interface. This work demonstrates a simple but efficient method to improve the TiO₂/perovskite interface that can be greatly beneficial for developing high-performance PSCs.

1. Introduction

Since the first report on perovskite solar cells (PSCs) in 2009 by Miyasaka et al., the power conversion efficiencies (PCEs) of PSCs have rapidly increased from approximately 3.8 to over 20% [1,2]. Two dominant device structures, known as mesostructured and planar heterojunction (PHJ) cells, have been employed to fabricate...
PSCs [3]. The most efficient PSCs employ mesoscopic metal oxides, such as TiO$_2$ or Al$_2$O$_3$, as a scaffold. The mesoporous layer plays a critical role by facilitating the formation of a homogeneous perovskite film and reducing the contact resistance. Al$_2$O$_3$ is unable to assist in electron extraction due to its large bandgap, which suggests that perovskite itself transports electrons [4]. Hence, PHJ structures have attracted increasing interest due to their potential to simplify the fabrication process by eliminating the need for the high-temperature-sintered mesoporous layer [5]. In a heterojunction structure, with no mesoscopic scaffold, the interfacial connection between compact TiO$_2$ and perovskite plays an important role in improving the cell performance. Therefore, other methods must be employed to provide a smooth, continuous perovskite film and to suppress electron–hole recombination [6]. Interfacial engineering is considered an effective method for achieving high device performance for PHJ PSCs. Generally, engineering the interface between a compact TiO$_2$ layer and a perovskite layer provides several advantages, such as easier charge transfer from the perovskite to the electron-transport layer (ETL), less interfacial charge recombination, improved perovskite grains and a passivated TiO$_2$ surface [7].

Different methods for treating the surface of TiO$_2$ have been developed to improve the compatibility of the TiO$_2$/CH$_3$NH$_3$PbI$_3$ interface. Qin et al. [8] evaporated Cs$_2$CO$_3$ on a compact TiO$_2$ layer, and the corresponding PCE was increased from 8.0 to 11.1%. Shih et al. and Y. Ogomi et al. applied amino acids to modify the mesoporous TiO$_2$/CH$_3$NH$_3$PbI$_3$ heterojunction interface, and the PCE of the resulting PSCs increased from 8.35 to 12.02% and 8 to 10%, respectively [9,10]. Zuo et al. [7] used 3-aminopropanoic acid to modify the compact TiO$_2$/CH$_3$NH$_3$PbI$_3$ heterojunction, and the PCE increased from 11.96 to 15.67%. However, the area of their solar cell was 5.2 mm$^2$, which is substantially different from the typical cell area of 0.1 cm$^2$. Other treatments have been employed to modify the surface of TiO$_2$ layer, such as TiCl$_4$ and UV/O$_3$ treatment [11]. Therefore, it is still necessary to develop a simple, fast and efficient method for fabricating highly efficient perovskite solar cells with highly device stability and reproducibility.

Amino silanes are widely applied to improve the quality of active layers. Mallakpour et al. [12] used a 3-aminopropyltriethoxy silane coupling agent to modify the OH-rich surface of α-MnO$_2$ following hydrolysis. Krishnaiah et al. [13] grafted hydrolysed 3-aminopropyltriethoxysilane onto Hal nanotubes in a solution of water and ethanol. This type of surface modification method is very simple, which avoids the use of heat or a complex atmosphere. Owing to the enhanced adhesion between the compact TiO$_2$ and perovskite active layers, high-quality CH$_3$NH$_3$I$_3$ films can be fabricated using a one-step spin-coating method [11]. To the best of our knowledge, the use of 3-aminopropyl trimethoxy silane (APMS) in modifying the TiO$_2$ layer to improve the PCE of PSCs has not been reported previously.

In this work, we propose to modify the TiO$_2$/CH$_3$NH$_3$PbI$_3$ interface by introducing APMS, a type of amino silane, as a coupling agent. This approach enhanced the PCE of the PHJ PSCs from 13.45 to 15.79%, representing a 17.4% enhancement.

2. Material and methods

2.1. Material and reagents

Fluorine-doped tin oxide glass (FTO) was obtained from YingKou OPV Tech New Energy Co. Ltd. Acetone, isopropanol, n-butyl alcohol and APMS were obtained from Aladdin. Bis(pentane-2,4-dionato-O,O’)(bis(propan-2-olato)titanium, PbI$_2$, γ-butyrolactone (GBL), tert-butylpyridine (tBP) and lithium bis(trifluoromethylsulfonyl)imide (Li-TFSI) were purchased from Sigma-Aldrich. CH$_3$NH$_3$I and spiro-MeOTAD were purchased from Xi’an Polymer Light Technology Corp.

2.2. Preparation of the compact TiO$_2$ layer

The transparent conducting FTO substrates were cleaned sequentially with 20 min of ultrasonication in detergent, deionized water, acetone and isopropanol, followed by drying in a N$_2$ stream. Subsequently, the FTO substrate was placed in UV-irradiation instrument to remove residual organic matter. A compact TiO$_2$ precursor solution was synthesized using a sol–gel method, wherein 0.5 ml of bis(pentane-2,4-dionato-O,O’)(bis(propan-2-olato)titanium, PbI$_2$, γ-butyrolactone (GBL), tert-butylpyridine (tBP) and lithium bis(trifluoromethylsulfonyl)imide (Li-TFSI) were purchased from Sigma-Aldrich. CH$_3$NH$_3$I and spiro-MeOTAD were purchased from Xi’an Polymer Light Technology Corp.

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2.3. Modification of the TiO$_2$ layer by 3-aminopropyl trimethoxy silane hydrolysate

APMS was hydrolysed in an 80:20 w/w mixture of ethanol and deionized water at a concentration of 10% w/w and with acetic acid added at 5% w/w relative to the solvent. The FTO substrate with the compact TiO$_2$ layer was immersed into the hydrolysate, and the grafting reaction was sustained for 2 h [14]. After that, the TiO$_2$ layer with APMS hydrolysate was washed with water and then immersed into 0.5 mol l$^{-1}$ HI solution for 2 h. Subsequently, the treated compact TiO$_2$ layer was washed by deionized water and dried in a N$_2$ stream.

2.4. Fabrication of PSCs

MAI and PbI$_2$ were added into a mixture of GBL and DMSO (7:3 v/v) at 60°C for 12 h. The precursor solution was coated onto the TiO$_2$ layer with and without APMS modification at 5000 r.p.m. for 55 s. During the spin-coating process, the substrate was treated by chlorobenzene drop-casting [15]. The substrate was then dried on a hot plate at 100°C for 10 min. A spiro-MeOTAD solution was prepared by dissolving 72.3 mg of spiro-MeOTAD in 1.0 ml of chlorobenzene, into which 28.8 µl of tBP and 17.5 µl of a Li-TFSI solution (520 mg Li-TFSI in 1 ml acetonitrile, Sigma-Aldrich, 99.8%) were added. The spiro-MeOTAD solution was spin-coated onto the perovskite films at 5000 r.p.m. for 30 s. Finally, an Au electrode with a thickness of 80 nm was thermally evaporated onto the spiro-MeOTAD-coated substrates.

2.5. Characterization

The surface of bare compact TiO$_2$ (c-TiO$_2$) and APMS-hydrolysate-treated c-TiO$_2$ was investigated using X-ray photoelectron spectroscopy (XPS, ESCALAB-210) with Al K$_α$ radiation (1486.6 eV). The current density (J)–voltage (V) characteristics were measured with a computer-controlled Keithley 2400 under AM 1.5 illumination (100 mw cm$^{-2}$) from a Newport solar simulator. The incident photon-to-electron conversion efficiency (IPCE) was measured by a QEXL Solar Cell Spectral Response instrument. Contact angles were measured by a KRUSS DSA30. The morphology of c-TiO$_2$/perovskite and c-TiO$_2$/APMS-hydrolysate/perovskite was characterized using field emission scanning electron microscopy (FE-SEM, Hitachi S-4800). X-ray diffraction (XRD) patterns of the CH$_3$NH$_3$PbI$_3$ films were recorded on a HaoYuan DX-700 diffractometer. Capacitance–voltage (C–V) measurements and electrochemical impedance spectroscopy (EIS) were performed on an Electrochemical Workstation (VMP3, Bio-Logic, France).

3. Results and discussion

The n-i-p planar PSC structure with APMS hydrolysate between TiO$_2$ and CH$_3$NH$_3$PbI$_3$ layer is shown in figure 1a. Cross-sectional SEM image exhibits each functional layer in figure 1b. (HO)$_3$Si-R-NH$_3$I was expected to grow on the surface of the compact TiO$_2$ layer, in which NH$_3^+$ and I$^-$ moieties were incorporated into the surface of the CH$_3$NH$_3$PbI$_3$ layer, thus anchoring it to the perovskite layer [7,10].

As seen in figure 1b and electronic supplementary material, figure S1, no obvious modified layer can be observed. The APMS hydrolysate layer was considered as self-assembly monolayer or extremely thin layer, covering the TiO$_2$ surface [16]. To investigate the hydrolytic degree of APMS and the grafting onto the surface of the compact TiO$_2$ layer, X-ray photoelectron spectroscopy (XPS) was used to analyse the TiO$_2$ film before and after surface modification [17]. The XPS wide-scan survey spectra are shown in figure 2a. All of the peaks were calibrated using the C 1s peak (284.8 eV) as a reference [18]. Peaks of Si 2p, N 1s and I 3d can be clearly observed in the XPS spectra of TiO$_2$ before and after modification with APMS (indicated by rectangles in figure 2a). A detailed analysis of these XPS spectra provides clear evidence that the films were chemically modified, which was confirmed by the Si 2p, N 1s and I 3d spectra from fitted curves obtained using XPSPEAK software. As illustrated in figure 2b, the Si 2p peak was located at 102.07 eV following modification, while N 1s was at 401.25 eV (figure 2c), and the peak for I was located at 618.41 eV (figure 2d). Thus, the APMS hydrolysis product was clearly grafted onto the hydroxyl-rich TiO$_2$ layer.

The current density (J)–voltage (V) characteristics of the PSCs both without and with APMS hydrolysate modification, measured under reverse scan are shown in figure 3a. Table 1 shows the performance parameters of the two types of PSCs. The PCE of the solar cells increased from 13.45% when fabricated with a bare compact TiO$_2$ layer to 15.79% with the TiO$_2$ layer modified by APMS hydrolysate. Moreover, the $J_{sc}$ increased from 21.56 to 22.84 mA cm$^{-2}$, and the FF increased from 62.23 to 68.04%.
Figure 1. (a) Schematic of the perovskite solar cell with APMS hydrolysate inserted between the perovskite and compact TiO₂ layer. (b) Cross-sectional SEM image of the fabricated cell.

Figure 2. XPS spectrum of the films before and after modification with APMS hydrolysate. (a) XPS wide-scan survey, (b) Si 2p, (c) N 1s and (d) I 3d.

The photovoltaic properties of fabricated devices were examined under reverse and forward scan, as seen in electronic supplementary material, figure S2(a,b). Both devices exhibit hysteresis. The best PCE under reverse scans is 2.2–2.8% higher than those under forward scans. According to the forward and reverse statistic, it is evident that the hysteresis of the devices was reduced after APMS hydrolysate modification. The PCE of reverse scan was enhanced from 13.45 to 15.79%, it is a 27.3% enhancement, while the PCE of forward scan was enhanced from 10.65 to 13.56%, it is a 27.3% enhancement. Such a different enhancement in PCE was mainly due to the changing rate in FF gap between forward scan and reverse scan was decreased by inserting APMS hydrolysate. Fifty cells for each type of PSC were constructed, and a histogram of their PCEs is shown in figure 3b, which clearly demonstrates that the
fitted curve shifted right to a higher efficiency. This shift indicates that the average efficiency of the PSCs with modified compact TiO2 layers is higher than that of the cells with unmodified layers. Using another analysis method, the PCEs of PSCs modified with APMS hydrolysate exhibit an efficiency range of 10–15%, which is higher than that of unmodified cells, 8–13%. In order to further demonstrate the statistics, a PC60BM layer was introduced as an interface layer as reported [19–21]. As a control group, the only difference in the experiment was to replace APMS hydrolysate with PC60BM. PCBM solution was spin-coated onto the clean substrates at 6000 r.p.m. for 40 s. The cross-sectional SEM image is shown in electronic supplementary material, figure S1b. The best device obtained a PCE of 14.82% with a Voc of 1.0 V, a FF of 64.73% and a Jsc of 22.75 mA cm−2.

**Figure 3a** presents the incident photon-to-electron conversion efficiency (IPCE) spectra of the PSCs. The curves of all of the PSCs display a wide photoresponse from 350 to 800 nm, which is consistent with the absorption spectrum of CH3NH3PbI3. Photocurrent generation was initiated at 1.55 eV, which is in good agreement with the bandgap of CH3NH3PbI3 [22]. The integrated photocurrents estimated from the IPCE curve were 21.1 and 20.0 mA cm−2 for the two devices with and without APMS hydrolysate, respectively, which agree well with the values obtained from the J–V measurements. Moreover, the device with APMS hydrolysate obviously demonstrates higher IPCE values, especially in the range of 450–750 nm, as evidenced by the higher IPCE value exhibited at 500 nm (77.6%) related to its bare compact-TiO2 ETL-based counterpart (74.0%). This higher IPCE may benefit from more efficient electron collection and less charge recombination due to the insertion of APMS hydrolysate, thereby increasing the Jsc.

The contact angles of droplets of GBL on the modified and unmodified TiO2 films were measured to investigate the mechanism through which APMS hydrolysate improves the efficiency of the PSCs [23]. As shown in **Figure 4a,b**, the contact angle of GBL on the untreated TiO2 film is 23.83°, while the GBL spreads out on the APMS-hydrolysate-modified TiO2 film. These results suggest that the GBL wettability on TiO2 was enhanced.

SEM images of the perovskite on both the bare and modified TiO2 layers are shown in **Figure 4c,d**. The perovskite crystals on the modified TiO2 layer are more uniform than those on the bare TiO2 layer, and the crystals grown directly on the bare TiO2 surface exhibit a slightly smaller grain size than those grown.
on the modified surface. The morphological evolution of the perovskite film with APMS hydrolysate could be attributed to the improved miscibility of the substrate with the perovskite, wherein the amino group is expected to become ammonium and incorporate into the crystalline structure of the perovskite, as shown in figure 1. Larger grain sizes result in fewer grain boundaries for the photogenerated charges to traverse, thereby decreasing charge losses due to recombination at grain boundaries [24].

Figure 4e illustrates the X-ray diffraction (XRD) patterns of the CH$_3$NH$_3$PbI$_3$ films grown on TiO$_2$ both with and without APMS hydrolysate modification. The peaks at 14.1°, 28.4°, and 42.1° can be attributed to the (110), (220) and (330) faces of the CH$_3$NH$_3$PbI$_3$ crystalline structure, respectively [7]. The characteristic peaks appear at the same angles, indicating the pure perovskite phase on both surfaces without a change in the crystal orientation [25]. In addition, the diffraction peaks at 14.1° and 28.4° were significantly enhanced by APMS hydrolysate modification, indicating an improvement in the crystallinity of the CH$_3$NH$_3$PbI$_3$ film.

The steady-state PL spectra of the CH$_3$NH$_3$PbI$_3$ films are shown in figure 4f to illustrate the charge transport and dynamics of the corresponding devices fabricated on the c-TiO$_2$ layer without and with APMS hydrolysate treatment. The samples were excited at 440 nm, and both perovskite films exhibited an emissive band with a maximum at approximately 770 nm and a broad emission band ranging from 720 to 850 nm. With the introduction of APMS hydrolysate, a significant fluorescence quenching of perovskite is exhibited, which indicates enhanced electron transport from the perovskite to the APMS-hydrolysate-treated c-TiO$_2$ layer. This phenomenon demonstrates that the introduction of APMS hydrolysate could facilitate charge transfer between the perovskite and TiO$_2$ layer. Owing to the shorter diffusion length of electrons than that of holes in perovskite materials, efficient electron transfer and extraction balance the electron and hole transport in PSC devices, resulting in a significant enhancement of the FF [17].

The electronic trap states are able to delocalize charge carriers and induce high capacitance at the interface, which can be readily detected using impedance spectroscopy [25]. To further investigate the trap states on the compact TiO$_2$ surface both before and after modification, capacitance–voltage measurements were performed on the PSCs fabricated with and without APMS hydrolysate treatment at 1 kHz (figure 5a). At this frequency, the capacitance clearly varies with increasing bias voltage, which is indicative of charge accumulation at the compact layer and can thus reflect its capacitance [26]. As shown in figure 5a, the capacitances of devices treated with APMS hydrolysate are lower, confirming the passivation effect of APMS hydrolysate. The change in capacitance supports the speculation that fewer carriers gather in the traps and that a longer lifetime results in higher performing PSCs fabricated with APMS-hydrolysate-treated compact TiO$_2$.

To further investigate the effect of the APMS hydrolysate at the TiO$_2$/CH$_3$NH$_3$PbI$_3$ interface on the photovoltaic performance, electrochemical impedance spectroscopy (EIS) was employed to characterize the charge-transfer dynamics of PSCs by analysing the variation in the impedance related to the different
4. Conclusion

Modifying the interface between TiO$_2$ and perovskite layers by inserting APMS hydrolysate was demonstrated to enhance the photovoltaic performance of solution-processed PHJ PSCs. The PCE improved from 13.45 to 15.79% (representing the best solar cells), and the average PCE increased from 12.01 to 14.20%, thus confirming the desired effect of APMS hydrolysate. First, the wettability of GBL on the TiO$_2$ surface was enhanced, and as a result, the CH$_3$NH$_3$PbI$_3$ precursor solution spread out over the compact TiO$_2$ layer. Second, perovskite crystals were larger and more uniform on the modified layer. The surface traps of TiO$_2$ could be passivated by the APMS hydrolysate, and a portion of the molecule was believed to have incorporated into the perovskite crystal. Third, EIS tests revealed that the recombination resistance of the TiO$_2$/perovskite interface increased. Our work highlights the effects of APMS hydrolysate on the performance of the TiO$_2$/perovskite heterojunction in PHJ PSCs.

Data accessibility. The datasets supporting this article have been uploaded as the electronic supplementary material. Our data have been deposited in the Dryad Digital Repository: https://doi.org/10.5061/dryad.8s544 [31].

Authors’ contributions. Y.-Q.W. performed the experiments, collected data and drafted the manuscript. Y.-Q.W. and S.-B.X. conceived of and designed the study. J.-G.D. and L.-Z.G. coordinated the study and revised the manuscript. All authors gave final approval for publication.

Competing interests. The authors declare no competing interests.

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