Research Article

Effect of Modulating Spin-Coating Rate of TiO_2 Precursor for Mesoporous Layer on J - V Hysteresis of Solar Cells with Polar $\text{CH}_3\text{NH}_3\text{PbI}_3$ Perovskite Thin Film

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Compared with the crystalline Si solar cells, the J - V characteristics of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells are different under forward and reverse scan, and the $\text{CH}_3\text{NH}_3\text{PbI}_3$ film exhibits some polarization properties. To explore those performances of the mesoporous TiO_2 layer based perovskite solar cells, we focus on the effect of modulating the spin-coating rate of the TiO_2 precursor for mesoporous layer on J - V hysteresis of solar cells with the polar film by J - V curves, atomic force microscopy topographic images, and piezoresponse force microscopy phase images. Firstly, the AFM images illustrate that the polarization behaviors exist and the deformation scale is large at the corresponding position when the DC bias voltage increases. Secondly, it is suggested that the polar films which applied the positive DC biases voltage show a tendency to 0° phase angle, while the polar films which applied the negative DC biases voltage show a tendency to -180° phase angle. Thirdly, a weak polar hysteresis loop relation for $\text{CH}_3\text{NH}_3\text{PbI}_3$ film was observed. Finally, the hysteresis index for the 1500 rpm mesostructured solar cell shows relatively low J - V hysteresis compared with the 3000 rpm mesostructured and the planar-structured solar cell. Our experimental results bring novel routes for reducing the hysteresis and investigating the polar nature for $\text{CH}_3\text{NH}_3\text{PbI}_3$ material.

1. Introduction

Aiming at next-generation solar cells, the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite as a light harvester has been widely used in solar cells owing to its low cost and outstanding desirable properties [1]. Currently, the efficiency, stability, and large area of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells are the main focuses, while the polarization behaviors of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite film and J - V hysteresis of $\text{CH}_3\text{NH}_3\text{PbI}_3$ -based perovskite solar cells receive insufficient attention and evolve slowly. Dualeh et al. first reported the J - V hysteresis of $\text{CH}_3\text{NH}_3\text{PbI}_3$ -based perovskite solar cells [2]. Snaith et al. reported effect of three factors including scan rate, architectures, and mesoporous components on hysteresis [3]. Tress et al. reported the role of a compensated electric field on the rate-dependent J - V hysteresis [4]. O'Regan et al. reported an evolution in band offset at the $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3$ interface

during J - V Hysteresis [5]. Meloni et al. investigated the origin of this phenomenon with a combined experimental and computational approach [6]. Kutes et al. showed the presence of ferroelectric domains in high-quality β - $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite thin films that have been synthesized using a new solution-processing method [7]. Kim and Park investigated effects of perovskite crystal size and mesoporous TiO_2 layer on J - V Hysteresis of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells [8]. Then they reported on ferroelectric polarization behavior in $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite in dark and under illumination [9]. Coll et al. reported on polarization switching and light-enhanced piezoelectricity in lead halide perovskites [10]. The low conductivity of the contact materials (TiO_2 or HTMs) is one of reasons for the high J - V hysteresis [11, 12].

In this work, we have investigated the polarization behaviors and local hysteresis phenomenon of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ films, as well as the polarization orientation by AFM and

PFM. In addition, a weak polar hysteresis loop between the polarization and the external electric field of FS and RS for $\text{CH}_3\text{NH}_3\text{PbI}_3$ film was observed. We also study the effect of spin-coating rate of TiO_2 precursor for mesoporous layer on HI of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells.

2. Experimental and Methods

2.1. Materials. Unless stated otherwise, all materials were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd., or Shanghai MaterWin New Materials Co., Ltd., and used as received. Co(III) PF₆ Spiro (spiro-OMeTAD) solution was purchased from Beijing HuaMin New Materials Technology Co., Ltd.

2.2. Device Fabrication. The fluorine-doped tin oxide (FTO) conductive glasses were cleaned by ultrasonic in detergent, rinsed with deionized water, followed by washing with the mixture of deionized water, ethanol, and acetone at 1:1:1 by volume, and suffered from an O_3 /ultraviolet treatment for one hour. The TiO_2 blocking (bl- TiO_2) underlayer was deposited on the cleaned FTO conductive glasses by spin-coating method at 2000 rpm for 30 s and sintered at 500°C for 30 min.

In our trials, the following two parts were carried out. (1) In terms of polarization behaviors measurements, we took the FTO/bl- TiO_2 /mp- TiO_2 / $\text{CH}_3\text{NH}_3\text{PbI}_3$ mesostructured device and the FTO/bl- TiO_2 / $\text{CH}_3\text{NH}_3\text{PbI}_3$ planar structured device for measurements. A TiO_2 paste was diluted by ethanol at 2:7 by weight to prepare the mp- TiO_2 precursor. The mp- TiO_2 precursor was deposited on top of the FTO/bl- TiO_2 substrates with the spin-coating rates for 3000 rpm and 1500 rpm for 30 s and sintered at 500°C for 30 min to form mp- TiO_2 layers. The perovskite films were prepared by two-step sequential deposition method [14]. The PbI_2 (1 mol/L) solution which was stirred for one hour at 70°C was deposited on the mp- TiO_2 film at 5500 rpm for 15 s, followed by thermal annealing at 100°C for 30 min on hot plate to form a stable film. The PbI_2 solution was kept at 70°C while spin-coating. The methylammonium iodide solution (MAI 10 mg/ml dissolved in 2-isopropanol) was spin-coated on top of PbI_2 layers at 0 rpm for 10 s, followed by 3000 rpm for 30 s to form $\text{CH}_3\text{NH}_3\text{PbI}_3$ films, and then the as-fabricated films were dried at 100°C for 30 min. (2) In terms of the hysteresis in J - V measurements, we took the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells with different thickness mp- TiO_2 layers and without mp- TiO_2 layers for measurements. To prepare the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells, the following steps were carried out. The spiro-OMeTAD solution was deposited on top of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films by spin-coating at 2000 rpm for 30 s. Finally, a candle burning method was used to prepare carbon electrode as counter electrode. The FTO-candle soot film was directly deposited by putting a cleaned FTO glass in the candle flame for about 3 s [15]. Then the FTO-candle soot film and the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite film were directly clamped to fabricate the solar cell.

2.3. Characterization. The J - V curves were measured by a VersaSTAT3 source meter under standard air-mass 1.5

global (AM 1.5G) illumination ($100 \text{ mW}\cdot\text{cm}^{-2}$) provided by a solar simulator (Oriel Sol 3A). The monochromatic incident photon-to-electron (IPCE) was measured with an IPCE measurement tool (Institute of Physics, CAS, China) in our laboratory. 3D surface topography AFM images were obtained by Dimension AFM (Bruker). PFM measurements require NanoScope software 7.20 R1 SR1 with the NanoScope V Controller using a Dimension AFM (Bruker). The photoluminescence (PL) diagrams were obtained by the LabRAM HR800, which was made by HORIBA Jobin Yvon. The ultraviolet-visible (UV-Vis) absorption spectrums were obtained by the test system, which consisted of AvaSpec-ULS2048XL, test software, AvaLight-DH-S-BAL as a light source, AvaSphere-50-REFL, AvaSphere-IRRAD, and so on.

3. Results and Discussions

3.1. 3D Surface Topography AFM Images Illustrate the Polarization Behaviors and Local Hysteresis Phenomenon of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ Films. To investigate the polarization behaviors and local hysteresis phenomenon of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ films, the topography and the dielectric response of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ films were measured by AFM.

A dielectric can be polarized by an applied electric field. When a dielectric is placed in an electric field, electric charges do not flow through the material but only slightly shift from their average equilibrium positions causing dielectric polarization. Because of dielectric polarization, positive charges are displaced toward the field and negative charges shift in the opposite direction [16].

In AFM images, the DC bias voltage applied an electric field, which is capable of rotating the orientation of the polarization. Thus, it is dielectric polarization.

To understand the polarization behaviors of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films, we applied a DC bias voltage between the $\text{CH}_3\text{NH}_3\text{PbI}_3$ film and the conductive tip during the AFM measurement; the DC biases voltages were set to 0 V, +3 V, +6 V, and -10 V, respectively. In addition, for poling the samples, an AC voltage was applied from the conductive tip to the film's surface during the AFM and PFM measurements.

We take the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films with the spin-coating rate of the mp- TiO_2 precursor for 1500 rpm as the typical sample for the AFM measurement. Figures 1 and 2 are the same substrate. Figures 1(a), 1(b), 1(c), and 1(d) are the same substrate and the same position, and Figures 2(a) and 2(b) are the same substrate and the same position. In order to see clearly, Figures 1(c) and 1(d) are the enlargement of the center of Figures 1(a) and 1(b). Because when applying negative DC voltage of -10 V, a distortion may occur. The same substrate and the same position were selected for Figures 2(a) and 2(b). Figure 1 shows the 3D surface topography AFM images of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films with mp- TiO_2 layer which applied different DC bias voltage and AC voltage groups. The contrast of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films in 3D surface topography AFM images varies depending on the height of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite crystals; that is, the brighter the color of AFM image, the higher the peak on the surface of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite layer; in contrast, the darker the color of AFM image, the deeper the valley

FIGURE 1: 3D surface topography AFM images of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films with mp-TiO₂/bl-TiO₂/FTO structure which applied DC biases voltage and AC voltage groups are (a) (0 V, 0 V), (b) (~ 8 V, 0 V), (c) (~ 8 V, +3 V), and (d) (~ 8 V, +6 V). (a), (b), (c), and (d) are the same substrate and the same position. In order to see clearly, (c) and (d) are the enlargement of the center of (a) and (b).

on the surface of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite layer. Compared with the sample which applied (0 V, 0 V) (Figure 1(a)), the surface topography of the samples is more uneven with the increasing of applied (~ 8 V, 0 V) (Figure 1(b)) and (~ 10 V, 0 V) (Figure 2(a)) AC voltage, because the AC voltage provides the energy of the vibration of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films, resulting in deformations. Huang et al. stated that the piezoresponse originates only from the polarization induced by the crystal structure deformation because of the applied AC bias [17]. When a DC bias voltage (+3 V) (Figure 1(c)) is applied, the surface topography of the sample has a clearly significant polarization behavior in the $\text{CH}_3\text{NH}_3\text{PbI}_3$ film. Furthermore, with the DC bias voltage increasing to +6 V (Figure 1(d)), the polarization behavior is stronger at

the corresponding position in 3D surface topography AFM images. Moreover, when the voltage group is increased to (~ 10 V, -10 V) (Figure 2(b)), a serious distortion occurs, because the breakdown voltage of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ film we fabricated is lower than 10 V. These results presented here demonstrate that the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films have a scale of vertical deformation under the DC bias voltage and AC voltage groups, and the deformation scale is large at the corresponding position when the DC bias voltage increases. Huang et al. stated that when the bias field strength exceeded a certain threshold, a permanent breakdown occurred in CdS/CdTe film [17]. In this work, similarly, when applying negative DC voltage of -10 V on perovskite film, a serious distortion occurred in AFM images. According to the AFM

FIGURE 2: DC biases voltage and AC voltage groups are (a) (~ 10 V, 0 V) and (b) (~ 10 V, -10 V). Figures 2(a) and 2(b) are the same substrate and the same position.

FIGURE 3: Vector diagram of E field and sample oscillation vectors for (a) 0° and (b) 90° drive phase [13].

image, we infer that the -10 V is probably up to breakdown voltage. The deformation is reversible if the voltage applied is below or far below the breakdown voltage. When the voltage applied is higher or much higher than the breakdown voltage, the distortion is not reversible. Huang et al. reported that CdS/CdTe film can withstand a large bias field which could reach 8×10^4 V/cm; this suggests that there is less possibility of electrical failures during future applications [17]. In our work, in terms of perovskite film, it can bear 6 V in our experiments, if we take ~ 500 nm for its thickness, perovskite film can withstand a larger bias field of 1.2×10^5 V/cm. So there is less possibility of electrical failures during future applications of the perovskite solar cells.

3.2. Effect of Spin-Coating Rate of TiO_2 Precursor for Mesoporous Layer and Additional DC Bias Voltage on the PFM Phase Orientation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ Films. Two vector diagrams, shown in Figure 3, illustrate a number of properties of

the digital lock-ins, without going into the details of the actual lock-in implementation. The digital lock-in implementation phase angle varies between -180 and $+180$ degrees, not 0 to 360 degrees, and the raw outputs of the lock-ins are the inphase and quadrature values [13].

The $\text{CH}_3\text{NH}_3\text{PbI}_3$ films were deposited on the FTO/bl- TiO_2 substrates without the mp- TiO_2 layer and the FTO/bl- TiO_2 /mp- TiO_2 substrate with the spin-coating rates of the mp- TiO_2 precursor for 1500 rpm and 3000 rpm, respectively.

We can compare contrast in PFM image with the scale bar. The contrast in PFM image represents the tendency of the polarization. In order to further investigate the polarization-switching behaviors, the switching measurements were performed by applying positive biases voltage of +3 V and +6 V and negative biases voltage of -3 V and -6 V to the conductive tip. The orientation of the polarization of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films can be characterized by the corresponding PFM phase images. To estimate the

FIGURE 4: PFM phase images of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films which applied (0 V, 0 V) (a) w/o mp- TiO_2 layer and (b) with the spin-coating rate of the mp- TiO_2 precursor for 3000 rpm and (c) with the spin-coating rate of the mp- TiO_2 precursor for 1500 rpm. PFM phase images of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films which applied (~ 8 V, 0 V) (d–f) correspond to those which applied (0 V, 0 V) without mp- TiO_2 layer and with the different spin-coating rates of the mp- TiO_2 layers.

effect of mp- TiO_2 layer on the polarization behaviors, the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films with planar structure (w/o mp- TiO_2 layer) and mesoporous structure (with the spin-coating rates of the mp- TiO_2 precursor for 3000 rpm and 1500 rpm, resp.) were selected as samples for the PFM measurements. Note that overall $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite thin film is fabricated by the same preparation process for all devices regardless of mp- TiO_2 layer.

The PFM phase images of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films which applied (0 V, 0 V) without mp- TiO_2 layer and with the different spin-coating rates of the mp- TiO_2 layers are depicted in Figures 4(a)–4(c), which implies the absence of polarization in $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films in the absence of electric field. When the samples applied an AC voltage of ~ 8 V (Figures 4(d)–4(f)), it is found that the stimulated polarization shows a slight enhancement. Moreover, the sample with the spin-coating rate of the mp- TiO_2 precursor for 1500 rpm shows the strongest polarization compared to other samples.

Figure 5 shows the PFM phase images of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films which applied (~ 8 V, +3 V)

and (~ 8 V, +6 V) without mp- TiO_2 layer and with the different spin-coating rates of the mp- TiO_2 precursor. Compared with the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films which applied (~ 8 V, +0 V) (Figures 4(d)–4(f)), PFM phase images of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films show a clear distinction in the presence of an additional DC bias voltage of +3 V (Figures 5(a)–5(c)). Furthermore, the DC bias voltage of +6 V (Figures 5(d)–5(f)) is advantageous to the enhancement of the stimulated polarization. Interestingly, the positive DC bias voltage is capable of rotating the orientation of the polarization, which has a tendency to 0° phase angle. Besides, the higher positive DC bias voltage (+6 V) is beneficial to the enhancement of the tendency. Additionally, despite +3 V or +6 V of the positive DC biases voltage, the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite film with the spin-coating rate of the mp- TiO_2 precursor for 1500 rpm shows the most promising tendency to 0° phase angle among these samples.

Figure 6 shows the PFM phase images of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films which applied (~ 8 V, –3 V) and (~ 8 V, –6 V) without mp- TiO_2 layer and with the different spin-coating rates of the mp- TiO_2 precursor.

FIGURE 5: PFM phase images of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films which applied (~ 8 V, +3 V) (a) w/o mp- TiO_2 layer and with the spin-coating rate of the mp- TiO_2 precursor for (b) 3000 rpm and (c) 1500 rpm. PFM phase images of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films which applied (~ 8 V, +6 V) (d–f) correspond to those which applied (~ 8 V, +3 V) without mp- TiO_2 layer and with the different spin-coating rates of the mp- TiO_2 precursor.

Similar stimulated polarization behavior is observed showing the capacity of rotation (Figures 6(a)–6(f)) compared to the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films which applied positive DC biases voltage (Figures 5(a)–5(f)) except for the orientation of the polarization, which has a tendency to -180° . Besides, the films which applied the negative DC bias voltage of -6 V (Figures 6(d)–6(f)) show a stronger polarization than the films which applied -3 V (Figures 6(a)–6(c)). In addition, regardless of -3 V or -6 V of the negative DC biases voltage, the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite film with the spin-coating rate of the mp- TiO_2 precursor for 1500 rpm shows the most promising tendency to -180° phase angle among these samples.

As a comparison of Figures 5 and 6, it is suggested that the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films which applied the positive DC biases voltage (Figure 5) show a tendency to 0° phase angle, while the films applied the negative DC biases voltage (Figure 6) showing a tendency to -180° phase angle. Moreover, the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite film which applied +6 V and -6 V bias with the spin-coating rate of the mp- TiO_2 precursor for 1500 rpm shows the most promising tendency to 0° and -180° phase angle, respectively.

3.3. A Weak Polar Hysteresis Loop Relation between the Polarization and the External Electric Field of FS and RS for $\text{CH}_3\text{NH}_3\text{PbI}_3$ Film. Figure 7 shows a weak polar hysteresis loop relation between the polarization and the external electric field of FS and RS. In this measurement, a DC bias varying between -6 V and $+4$ V was applied between the $\text{CH}_3\text{NH}_3\text{PbI}_3$ film and the conductive tip, in addition to the 8 V AC bias. As shown in Figure 7, a DC bias varying between -6 V and $+4$ V changes the phase orientation of the polarization from about 110° to -65° phase angle, which indicates that the DC bias voltage is capable of rotating the orientation of the polarization. Moreover, the separated curves of FS and RS are reasonable to infer that the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite could potentially be a polar material.

3.4. Effect of Spin-Coating Rate of TiO_2 Precursor for Mesoporous Layer on HI of $\text{CH}_3\text{NH}_3\text{PbI}_3$ Perovskite Solar Cells. Figures 8(a)–8(c) show the J - V curves of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells incorporating mp- TiO_2 layers with different spin-coating rates for 3000 rpm and 1500 rpm together with a planar structure without mp- TiO_2 layer, and their J - V curves depend on voltage sweep direction. Owing to

FIGURE 6: PFM phase images of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films which applied ($\sim 8\text{ V}$, -3 V) (a) w/o mp- TiO_2 layer and with the spin-coating rate of the mp- TiO_2 precursor for (b) 3000 rpm and (c) 1500 rpm. PFM phase images of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films which applied ($\sim 8\text{ V}$, -6 V) (d–f) correspond to those which applied ($\sim 8\text{ V}$, -3 V) without mp- TiO_2 layer and with the different spin-coating rates of the mp- TiO_2 precursor.

FIGURE 7: Phase-voltage curve of the typical $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite film, collected by PFM at the fixed conductive tip with DC bias from -6 V to $+4\text{ V}$ and AC bias of 8 V .

the hysteresis in J - V measurements, it is crucial to report both RS and FS measurements. It is noted that the J - V measurements are performed in both RS and FS directions at a scan rate of 0.1 V/s and overall back contact is carbon electrode, as well as under simulated AM1.5G (100 mW/cm^2 irradiation). Moreover, we also present IPCE spectrums and the integrated J_{sc} of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells depending on their corresponding films (Figures 8(d)–8(f)). As shown in Figures 8(d)–8(f), the integrated J_{sc} proved by IPCE measurement is in good agreement with that derived from the J - V measurements (Table 1).

Figures 9(a)–9(c) show the HIs of six perovskite solar cells with planar structure (w/o mp- TiO_2 layer) and mesoporous structure (the spin-coating rates of the mp- TiO_2 precursor for 3000 rpm and 1500 rpm, resp.). And Figures 9(d)–9(f) show the PCEs. The figures showed good reproducibility of the J - V hysteresis and J - V characteristics of the devices.

Here reported modified HIs are defined by

$$\text{HI} = \frac{J_{\text{RS}}(0.8V_{\text{oc}}) - J_{\text{FS}}(0.8V_{\text{oc}})}{J_{\text{RS}}(0.8V_{\text{oc}})}, \quad (1)$$

FIGURE 8: J - V curves of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells with (a) planar structure and the spin-coating rate of the mp-TiO₂ precursor for (b) 3000 rpm and (c) 1500 rpm. The corresponding IPCE spectrum and the integrated short circuit current density (J_{sc}) of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells with (d) planar structure and the spin-coating rate of the mp-TiO₂ precursor for (e) 3000 rpm and (f) 1500 rpm.

TABLE 1: Solar cell performance parameters w/o mp-TiO₂ layer or with the spin-coating rates of the mp-TiO₂ precursor for 3000 rpm and 1500 rpm.

	HI ($0.8V_{oc}$)	J_{sc} (mA cm^{-2})	V_{oc} (mV)	FF	PCE (%)
RS (planar)	0.611	3.01	918	0.37	1.03
FS (planar)		3.21	866	0.11	0.31
RS (3000 rpm)	0.255	9.07	813	0.65	4.82
FS (3000 rpm)		8.70	804	0.49	3.44
RS (1500 rpm)	0.181	10.01	847	0.58	4.93
FS (1500 rpm)		9.77	826	0.46	3.73

FIGURE 9: HIs of six perovskite solar cells with (a) planar structure and the spin-coating rate of the mp-TiO₂ precursor for (b) 3000 rpm and (c) 1500 rpm. PCEs of six perovskite solar cells with (d) planar structure and the spin-coating rate of the mp-TiO₂ precursor for (e) 3000 rpm and (f) 1500 rpm.

where $J_{RS}(0.8V_{oc})$ and $J_{FS}(0.8V_{oc})$ represent photocurrent density at 80% of V_{oc} for the RS and FS, respectively [8].

The HIs for CH₃NH₃PbI₃ perovskite solar cells were calculated by (1). As shown in Table 1, the HIs by (1) are calculated to be 0.611, 0.255, and 0.181, for planar structure without mp-TiO₂ layer, the spin-coating rates of the mp-TiO₂ precursor for 3000 rpm and 1500 rpm, respectively. Compared with the planar structure without mp-TiO₂ layer, the HI for the mesostructured device with mp-TiO₂ layer is smaller, which indicates that the mp-TiO₂ layer reduces the hysteresis. Meanwhile, the HI for the 1500 rpm mesostructured device is smaller than that for 3000 rpm, which indicates that the mp-TiO₂ layer for 1500 rpm has smaller J - V hysteresis than that for 3000 rpm. It is reasonable to believe that the relatively

low spin-coating rate in a proper range of mp-TiO₂ precursor reduces the hysteresis. Thus, the interface difference between mp-TiO₂ (1500 rpm and 3000 rpm) and perovskite is the main reason for the different hysteresis.

Figure 10(a) shows that three PL diagrams with the main PL peaking at 750~800 nm are attributed to the intrinsic band gap of approximate 1.6 eV from the CH₃NH₃PbI₃ crystal lattice [18]. The structure of planar device is glass/FTO/bl-TiO₂/CH₃NH₃PbI₃. The mesostructured device is glass/FTO/bl-TiO₂/mp-TiO₂/CH₃NH₃PbI₃. Planar structure device is different from mesoporous structure device in structure, so we do not compare their PL intensity, and we just take the planar structure as a reference. Compared with the PL intensity for 1500 rpm, the PL intensity for 3000 rpm is higher,

FIGURE 10: (a) PL diagram and (b) UV-Vis absorption spectrum of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite thin films with planar structure and the spin-coating rates of the mp- TiO_2 precursor for 1500 rpm and 3000 rpm.

which is in good agreement with the J - V measurements. Jiang et al. provided the PL diagrams of glass/perovskite and glass/bl- TiO_2 /perovskite. A higher PL intensity was observed for glass/perovskite than glass/bl- TiO_2 /perovskite [19]. This is certainly a theoretical result because photo-generated electrons are more easily transferred to bl- TiO_2 layer than glass; thus, the radiation recombination of photo-generated electrons and holes with glass/bl- TiO_2 /perovskite structure is lower than glass/perovskite structure, so a lower PL intensity was observed for glass/bl- TiO_2 /perovskite structure than glass/perovskite structure.

In terms of absorption spectrum of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells shown in Figure 10(b), the mesostructured devices with mp- TiO_2 layer have better absorption than the planar structured device. In addition, the mesostructured device with mp- TiO_2 layer for 1500 rpm has the best absorption in our experiments. The mp- TiO_2 layer is a skeleton structure. The perovskite layer can grow in and on mp- TiO_2 layer. In the condition of the same method for perovskite formation, the perovskite layer is thick when the spin-coating rate of the mp- TiO_2 precursor is slow. The thicker the perovskite film is, the stronger the UV-Vis absorption behavior is.

Tripathi et al. reported their J - V curves of perovskite devices with different scan rates. Little difference of hysteresis exists with scan rates of 0.02 V/s, 0.05 V/s, 0.15 V/s, and 0.30 V/s [20]. Snaith et al. reported influence of scanning conditions on planar heterojunction perovskite solar cell current-voltage characteristics. A range of scan rates from 0.3 to 0.011 V/s was set. If scanned at 0.3 V/s it is possible to measure current-voltage curves without significant hysteresis [3]. The references indicate that J - V hysteresis may depend on the scan rates, while the appropriate scan rate is different in

different experiments. Thus, the high hysteresis obtained in this work is mainly due to the employed fast scan rate.

4. Conclusions

In summary, we investigated the effect of modulating spin-coating rate of TiO_2 precursor for mesoporous layer on J - V hysteresis of solar cells with polar $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite thin film. Firstly, the 3D surface topography AFM images illustrate the polarization behaviors and local hysteresis phenomenon of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ films. The result demonstrates that the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films have a scale of vertical deformation under the DC bias voltage and AC voltage groups, and the deformation scale is large at the corresponding position when the DC bias voltage increases. Secondly, we investigated the effect of spin-coating rate of TiO_2 precursor for mesoporous layer on the PFM phase orientation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films. It is suggested that the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films which applied the positive DC biases voltage show a tendency to 0° phase angle, while the negative DC biases voltage shows a tendency to -180° phase angle. Moreover, the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite film which applied +6 V and -6 V bias with the spin-coating rate of the mp- TiO_2 precursor for 1500 rpm shows the most promising tendency to 0° and -180° phase angle, respectively. Thirdly, a weak polar hysteresis loop relation between the polarization and the external electric field of FS and RS for $\text{CH}_3\text{NH}_3\text{PbI}_3$ film indicates that the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite could potentially be a polar material. Finally, the HI for the 1500 rpm mesostructured solar cell shows relatively low J - V hysteresis compared with the 3000 rpm mesostructured solar cell and the planar structured solar cell. Our experiments bring novel routes for the research of the $\text{CH}_3\text{NH}_3\text{PbI}_3$

perovskite material and $\text{CH}_3\text{NH}_3\text{PbI}_3$ -based perovskite solar cells. On the basis of our results, it may find its way into reducing the hysteresis and investigating the polar nature for $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite material.

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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