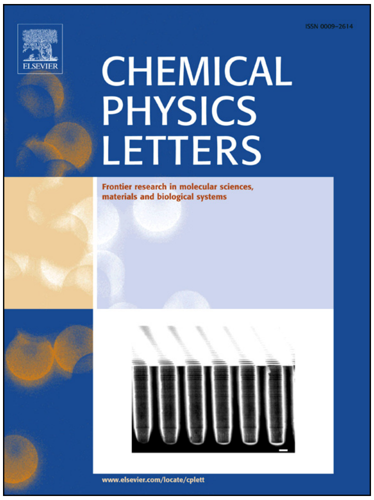

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# A New Layered Nano Hybrid Perovskite Film with Enhanced Resistance to Moisture-Induced Degradation

Wenlong Jiang[a,b], Jifei Ying[a], Wei Zhou[a], Kongchao Shen[b], Xing Liu[b], Xingyu Gao[b], Fuqiang Guo[c], Yanmin Gao[a]*, Tieying Yang[b]*

[a] *Jiangsu University of Science and Technology, Zhenjiang 100190, China*

[b] *Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201204, China*

[c] *Zhengzhou University of Industrial Technology, Zhengzhou, Henan 451150, China*

## Abstract

In this paper, a new layered hybrid perovskite film($(EDA)(MA)_2[Pb_3I_{10}]$) was synthesized through one-step method. Ethylenediamine(EDA) cation was introduced into the perovskite lattice to synthesize a layered structure with improved resistance to degradation by humidity. The effects of humidity and time on crystal structure, composition, morphology and absorption spectra of $(EDA)(MA)_2[Pb_3I_{10}]$ were analyzed by in situ grazing incidence X-ray diffraction(GIXRD), scanning electron microscope(SEM), and UV-Vis spectroscope. The results reveal that a $(EDA)(MA)_2[Pb_3I_{10}]$ film is more moisture resistant than a $CH_3NH_3PbI_3$ film which is widely used in the perovskite solar cell now. UV-Vis spectroscopy result also shows that the layered structure film is a suitable solar absorber with a bandgap(1.67 eV), which is close to the optimum value for solar photoelectric conversion. Compared to $CH_3NH_3PbI_3$, the low-cost perovskite structure offers greater tunability on a molecular level for further material optimization and possibility for widely used in the future.

## 1. Introduction

Solar energy is seen as one of the most promising renewable energy forms in the

21st century. The trend towards wide spread affordable use of solar energy has led to the development of thin-film based solar cells [1-2]. Perovskite solar cell has attracted increasing attention due to the superb photovoltaic performance thanks to the intrinsic material properties with high absorption coefficient, balanced charge transport behavior and low trap density. Since the first reports by Miyasaka et al in 2009, solar-cell-devices based on hybrid perovskites of the $CH_3NH_3PbX_3$ (X= I, Br, Cl) type have been largely improved as their power conversion efficiencies (PCEs) have drastically increased from 3.8 % to 22.1 % in only a few years [3-6]. However, the lead–halide perovskites have two main drawbacks: the toxicity of the water-soluble source of lead and the degradation of the material by atmospheric moisture [7]. After replacing the lead perovskite with the significantly less toxic tin analogue, solar cells reached efficiencies of up to about 6 % [8]. The moisture sensitivity, however, remains a major obstacle to commercialization. In the presence of high moisture, the degradation process and decay mechanism may be expressed as follows, which results in a significant decline in device performance [9].

In contrast to the 3-D perovskites, the layered two dimensional (2-D) systems can accommodate much larger and more complex organic cations. This is because the cage into which the organic cation must fit is no longer confined in three dimensions [10-12]. Karunadasa made devices using a layered perovskite $(PEA)_2(CH_3NH_3)_2[Pb_3I_{10}]$ as the absorber. The perovskite stucture showed no significant changes after a period of 46 days of exposure to humidity [13]. Alex M. Ganose synthesized a new layered perovskite struvture $(CH_3NH_3)_2Pb(SCN)_2I_2$, displaying improved chemical stability against phase separation when in high RH [14]. Here we reported a new layered perovskite $(EDA)(MA)_2[Pb_3I_{10}]$($EDA={}^{+}NH_3(CH_2)_2NH_3{}^{+}$,$MA=CH_3NH_3{}^{+}$) with enhanced resistance to moisture-induced degradation by combining $(EDA)I_2$, (MA)I, and $PbI_2$ in a 1:2:3 stoichiometric ratio in a solvent mixture of N,N-dimethylformamide(DMF). The successful preparation and application of the new layered perovskite material suggests that such materials may have a promising future in large-scale industrial applications.

## 2. Experimental

### 2.1 Materials

$(EDA)I_2$: HI solution was added dropwise to a cold(0 °C), stirred solution of Ethylenediamine(5.0 mL, 75 mmol) in ethanol(5.0 mL) until a colorless precipitate formed. The solid was filtered through paper and washed repeatedly with diethyl ether. Cooling a 60 °C, saturated isopropanol solution of the solid to 0°C afforded $(EDA)I_2$ in ca. 90 % yield. MAI(99%) was purchased from Materwin Techology from China.

$(EDA)(MA)_2[Pb_3I_{10}]$: Solid $(EDA)I_2$(73.4 mg, 0.289 mmol), (MA)I(92.0 mg, 0.578 mmol), and $PbI_2$(400 mg, 0.868 mmol) were dissolved in DMF(0.87 mL) at 60 °C for 6h and filtered through paper PTFE filters(0.45 mm) prior to use.

$MAPbI_3$: MAI and lead chloride ($PbI_2$, 99.99%, Alfa) powder were mixed in DMF (99.9%, Aldrich) with a molar ratio of 1:1. The perovskite precursor solution was stirred at 60 °C for 6h and filtered through PTFE filters (0.45 mm) prior to use.

### 2.2 Device fabrication

The $TiO_2$ compact film precursor solution in ethanol consists of 0.3 M titanium isopropoxide (Sigma-Aldrich, 99.999%) and 0.01M HCl. Dense $TiO_2$ film (≈40 nm) was coated onto F-doped $SnO_2$ (FTO) substrate by spinning titanium precursor at 5000 rpm, followed by annealing at 500 °C for 1 h. The precursor solution was deposited onto $TiO_2$/FTO substrate by spin-coating at 3000 rpm for 60 s. After drying the film on a hotplate at 100 °C for 0.5 h, the color of the film turned from yellow to dark brown, indicating the formation of perovskite. Subsequently, the spiro-OMeTAD (Sigma-Aldrich) solution (80 mg $mL^{-1}$ chlorobenzene) with 17.5 μL Li-bis(trifluoromethanesulfonyl) imide (Li-TFSI)/acetonitrile (500 mg $mL^{-1}$) and 28.5 μL TBP as additives was spin coated at 3000 rpm for 35 s. Finally, a 70 nm Au electrode was thermally evaporated as an electrode. All of the layers were fabricated inside an $N_2$-filled glove box.

### 2.3 Characterization methods

X-ray diffraction (XRD) including GIXRD was performed at BL14B1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF) using X-rays with a wavelength of 1.24 Å. The morphology of the films was studied using a JEOL PT008462 scanning electron microscope (SEM). The UV−vis absorption spectra of the thin films were measured with a Hewlett UV-3010 spectrophotometer. The J–V data were acquired with a Keithley 2400 source–meter unit. The light J–Vcurves were measured under illumination with a Newport-Oriel (Sol3A Class AAA Solar Simulator, 94043A) AM 1.5G light source operating at an intensity of 100 mW $cm^2$.

## 3. Results and discussion

Confirmation of the crystallographic data would be desirable to explore $(EDA)(MA)_2[Pb_3I_{10}]$. Crystal structure data obtained from one-dimensional (1D) powder X-ray diffraction provides only limited structural information, in particular for the highly oriented perovskite thin films. Therefore, we carried out in situ GIXRD measurements on the perovskite film that is subjected to about 80% RH. Snapshots of the in situ GIXRD experiments at various points in time are shown in Figure 1. All of the GIXRD patterns exhibited a relatively strong scattering background from the amorphous glass substrate in the range of q=10-25 $nm^{-1}$, where q is the scattering vector ($q=4\pi\sin(\theta)/\lambda$). After calibration, key features of the perovskite diffraction pattern could be observed at q≈10.04, 19.74 and 22.21 $nm^{-1}$. These are consistent with reflection from the (110), (220) and (310) lattice planes, respectively [15]. Fig 1(a) is the diffraction pattern of $(EDA)(MA)_2[Pb_3I_{10}]$ without water vapor around the sample, which reveals that the film is polycrystalline with preferred orientation along the normal direction. As shown in Fig. 2(b), with the time increasing in a relative humidity of 80 %, new features in the diffraction pattern at q≈9 $nm^{-1}$ become more and more intense and can be assigned to reflections from the (001) planes of $PbI_2$ (PDF#07-0235)[16].

According to Fig. 1(c) and Fig. 1(d), it can be found that, when the $CH_3NH_3PbI_3$ film was exposed to moisture, $PbI_2$ diffraction spots began to appear at q≈9 $nm^{-1}$. They eventually form a more complete ring pattern as the decomposition process continued and completed after 30 min. This suggests that the crystalline phase decomposes immediately when it is exposed to water vapor. On the other hand, for the

$(EDA)(MA)_2[Pb_3I_{10}]$ film – see Fig. 1(a),(b), little $PbI_2$ appears after 150 min and the crystalline phase does not decompose too much. So, $(EDA)(MA)_2[Pb_3I_{10}]$ film shows higher resistance to humidity than the $CH_3NH_3PbI_3$ film.

SEM images of $(EDA)(MA)_2[Pb_3I_{10}]$ and $CH_3NH_3PbI_3$ films were shown in Fig. 2 and differences on morphology between the two kinds of films could be seen clearly through SEM images. It could be seen from Fig. 2(a), by controlling the ratio of $(EDA)I_2$, (MA)I and $PbI_2$, we obtain the $(EDA)(MA)_2[Pb_3I_{10}]$ film which is in the form of flake microstructure and different layers are closely together with each other. While $CH_3NH_3PbI_3$ film is composed of independent micrometer-sized grains as shown in Fig. 2(b). External dense layer of $(EDA)(MA)_2[Pb_3I_{10}]$ film can protect inner layer from degradation and it consists with the GIXRD result that $(EDA)(MA)_2[Pb_3I_{10}]$ shows better resistance to high RH than $CH_3NH_3PbI_3$ films.

The contact angle is the angle at which a liquid meets a solid surface. Conventionally, the hydrophilicity and hydrophobicity of a surface is characterized by the contact angle (CA) of a single droplet of water on the surface. The larger angle represents better hydrophobicity. Fig. 3(a) shows the hydrophobic characteristics of the $CH_3NH_3PbI_3$ film according to the contact angle measurements. For this film, a small droplet of water (～8μL) formed a relatively hydrophilic contact, as indicated by the estimated CA of 40°. However, considerably higher hydrophobic behavior was observed on the film with the $(EDA)(MA)_2[Pb_3I_{10}]$ film, showing a CA of 73°, see Fig. 3(b), which is larger than for the $CH_3NH_3PbI_3$ film. Therefore, when faced with moisture, it can be seen that $CH_3NH_3PbI_3$ film would be influenced easier than the

$(EDA)(MA)_2[Pb_3I_{10}]$ film.

Fig. 4(a) showed that $(EDA)(MA)_2[Pb_3I_{10}]$ film had a good absorption in the visual light spectrum compared with $CH_3NH_3PbI_3$ films. Time-dependent changes of the optical properties of the $(EDA)(MA)_2[Pb_3I_{10}]$ and $CH_3NH_3PbI_3$ films were observed by recording light absorption spectra – see Fig. 4. The ex situ light absorption spectra of the $(EDA)(MA)_2[Pb_3I_{10}]$ film were measured immediately after the film preparations and after 5, 10, 15 and 20 days of storage at 35% RH. The ex situ light absorption spectra of the $CH_3NH_3PbI_3$ films were measured immediately after the film preparations and after 1, 2, and 3 days of storage in the same environment. As shown in Fig. 4(a), 17days later, the film had degraded only a little and still possessed good optical absorption. Eventually, the entire conversion of perovskite into $PbI_2$ was observed after approximately 30 days. The enhanced stability was confirmed again through visual observation. In contrast, as shown in Fig. 4(b), the $CH_3NH_3PbI_3$ films exhibit big changes of the absorption spectrum in short days at 35% RH due to dissolution-caused degradation. This shows a significantly weak stability with regard to humidity. All results suggest that a promising solution for overcoming the water sensitivity of the perovskite cell is replacing the $CH_3NH_3PbI_3$ with $(EDA)(MA)_2[Pb_3I_{10}]$. In addition, we also obtained the photoluminescence (PL) spectra of the $(EDA)(MA)_2[Pb_3I_{10}]$ film - see Fig. 4(a). We find a sharp PL peak at ~740 nm. This wavelength corresponds to the band gap energy of ～1.67 eV (according to the well-known relationship between band gap energy and wavelength: $EG = 1240/\lambda_{onset}$), and it is suitable for use as the light absorbing component.

Fig. 5(a) shows the J–V characteristic of device with (EDA)(MA)$_2$[Pb$_3$I$_{10}$] as the light absorber. The champion device exhibits a high Voc of 1.24 V, a Jsc of 16.57 mA cm$^{-2}$, and a FF of 0.56, yielding a PCE of 11.58 %. The encouraging result demonstrate that (EDA)(MA)$_2$[Pb$_3$I$_{10}$] is an efficient light absorber to obtain high-performance perovskite solar cells. In order to study the role of (EDA)(MA)$_2$[Pb$_3$I$_{10}$] in the device, we have designed a stability test using two samples based on CH$_3$NH$_3$PbI$_3$ and (EDA)(MA)$_2$[Pb$_3$I$_{10}$] as light absorber. As demonstrated in Fig. 5(b), the PCE of the perovskite solar cell with (EDA)(MA)$_2$[Pb$_3$I$_{10}$] drops only ~5 % after 18 days, which is much more stable than the CH$_3$NH$_3$PbI$_3$ one (~99 % drop). This experiment supports the importance of (EDA)(MA)$_2$[Pb$_3$I$_{10}$] in order to fabricate stable solar cells with high efficiency which could endure high RH.

## Conclusion

In summary, an EDA cation was introduced into the perovskite lattice to synthesize a layered structure with high resistance to moisture degradation. GIXRD result proves that the (EDA)(MA)$_2$[Pb$_3$I$_{10}$] film performs better than the CH$_3$NH$_3$PbI$_3$ film with regard to humidity caused degradation. Both water contact angle test and SEM measurement consist with the GIXRD result. UV-Vis absorbance spectroscopy result also indicates that the (EDA)(MA)$_2$[Pb$_3$I$_{10}$] film with a suitable band gap is an good replacement for the CH$_3$NH$_3$PbI$_3$ film when used as light absorption layer in solar cells. On the basis of this study, it could be possible to develop more stable PSCs using (EDA)(MA)$_2$[Pb$_3$I$_{10}$] films with the prospect of successful commercialization, perhaps after some additional complementing studies.

## Acknowledgments

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## Figure Captions

Fig. 1 2D GIXRD patterns of $(EDA)(MA)_2[Pb_3I_{10}]$ film on glass, after (a) 0 min (b) 150 min and $CH_3NH_3PbI_3$ film on glass, after (c) 0 min, (d) 30 min exposure to 80% RH.

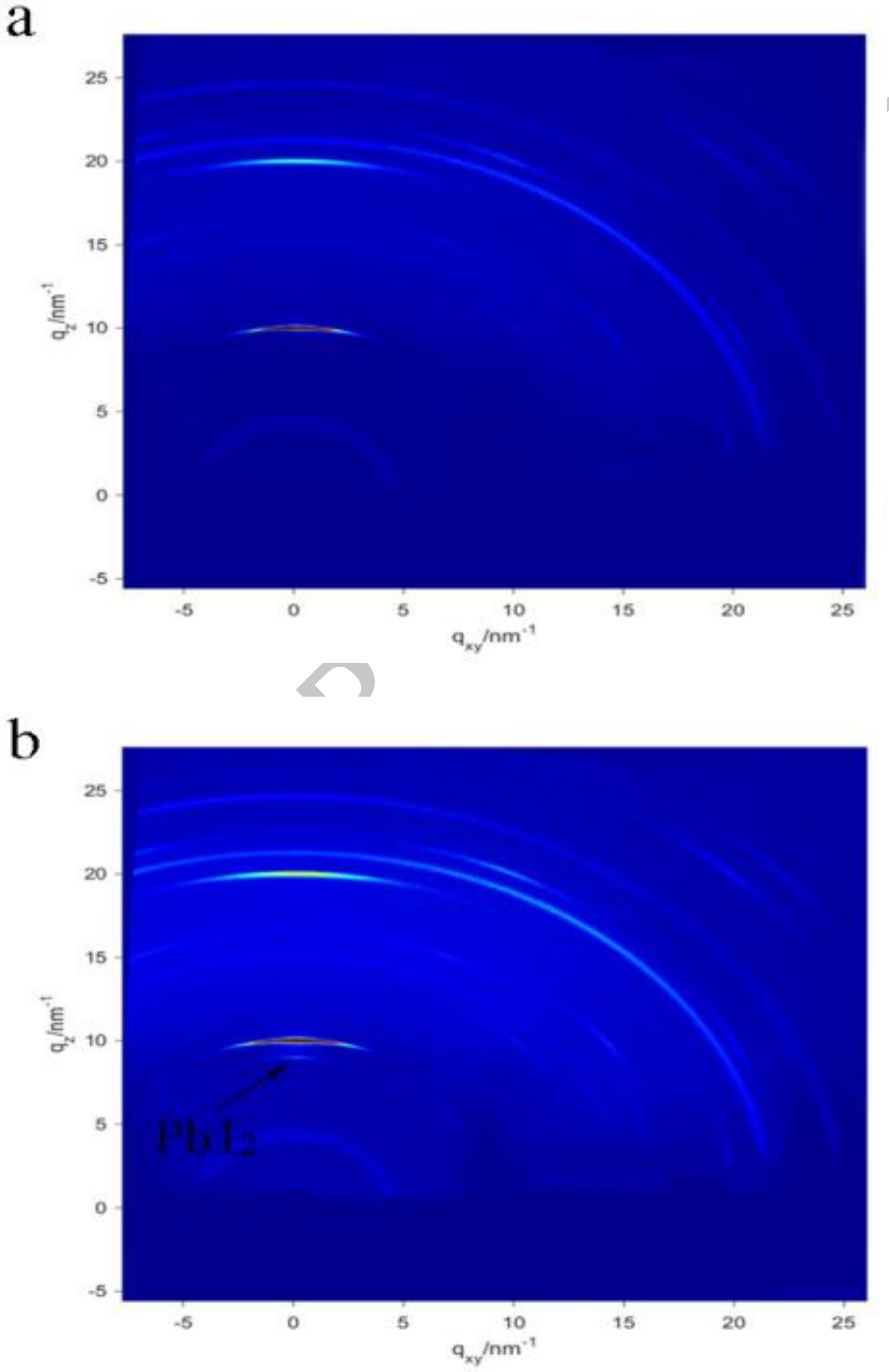
Fig. 2 SEM topography of (a) $(EDA)(MA)_2[Pb_3I_{10}]$ and (b) $CH_3NH_3PbI_3$ film

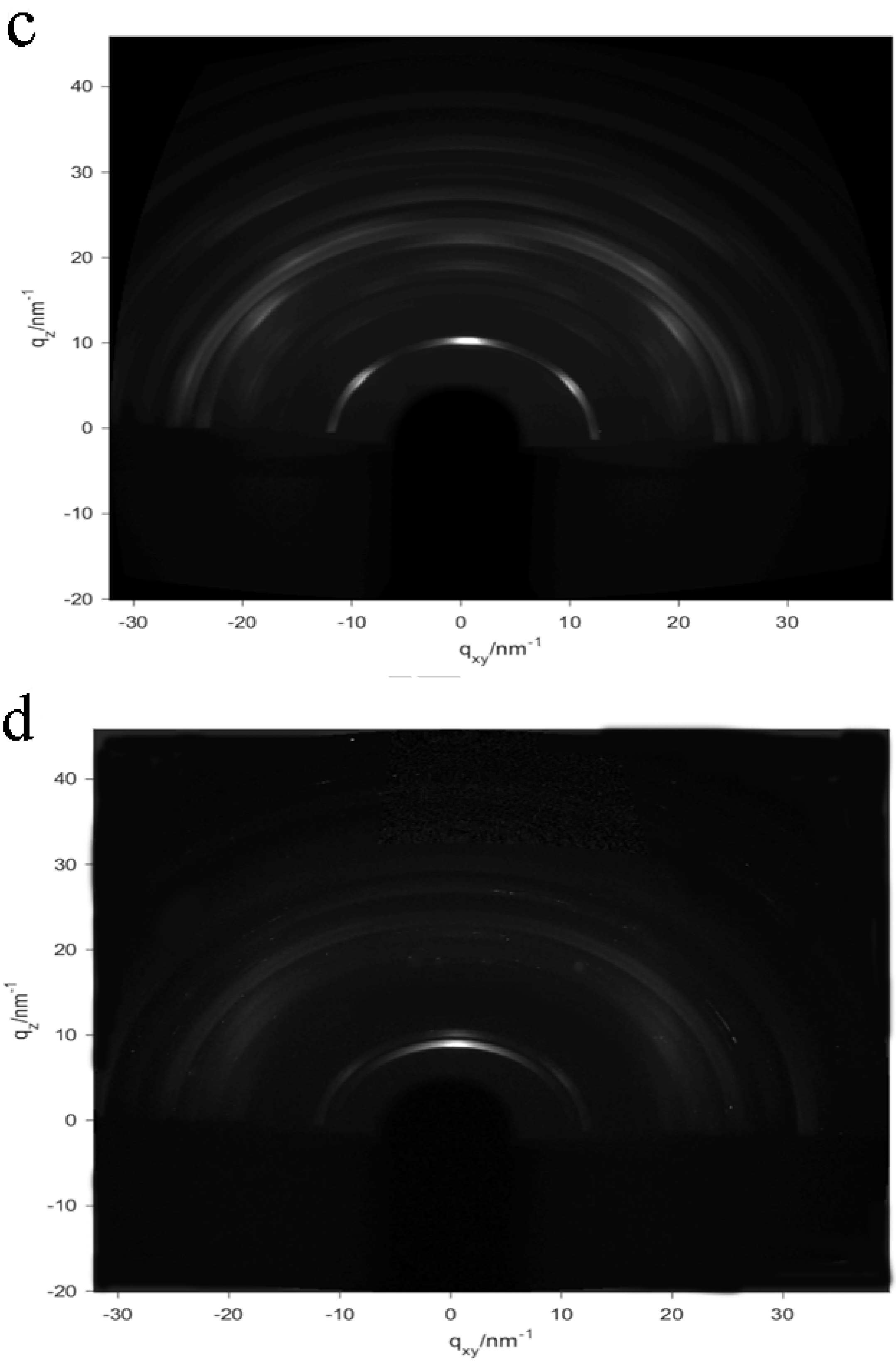
Fig. 3 Photograph of contact angle of water drop on (a) $CH_3NH_3PbI_3$ and (b) $(EDA)(MA)_2[Pb_3I_{10}]$ film surfaces

Fig.4 UV–vis absorption spectra for (a) $(EDA)(MA)_2[Pb_3I_{10}]$ and (b) $CH_3NH_3PbI_3$ films in a 35 % RH environment at different time point.

Fig.5 (a) J–V curves of solar cell with $(EDA)(MA)_2[Pb_3I_{10}]$ (b) Stability of the devices based on

(EDA)(MA)$_2$[Pb$_3$I$_{10}$] and CH$_3$NH$_3$PbI$_3$ in an ambient environment after encapsulation using UV-epoxy





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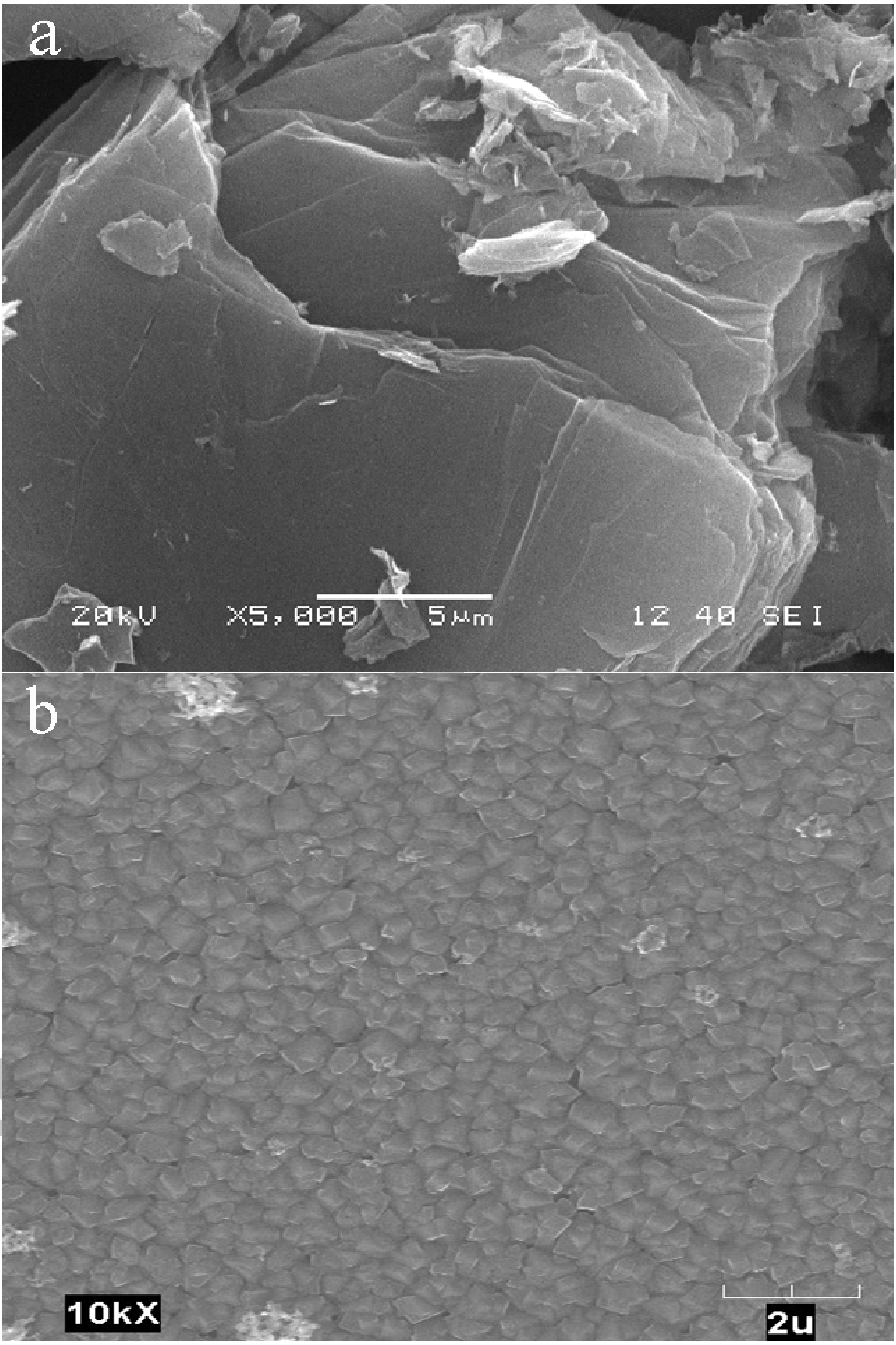

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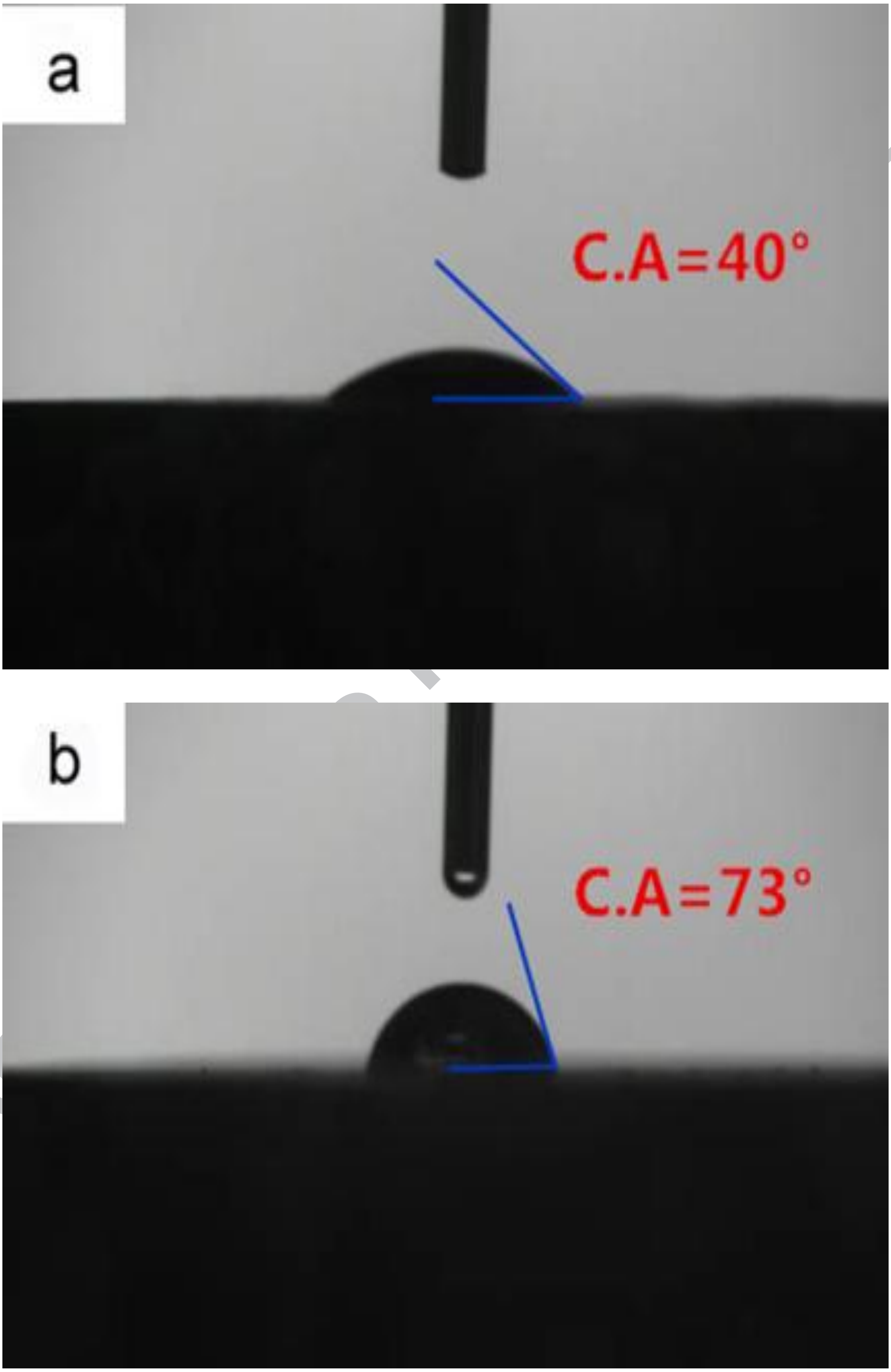

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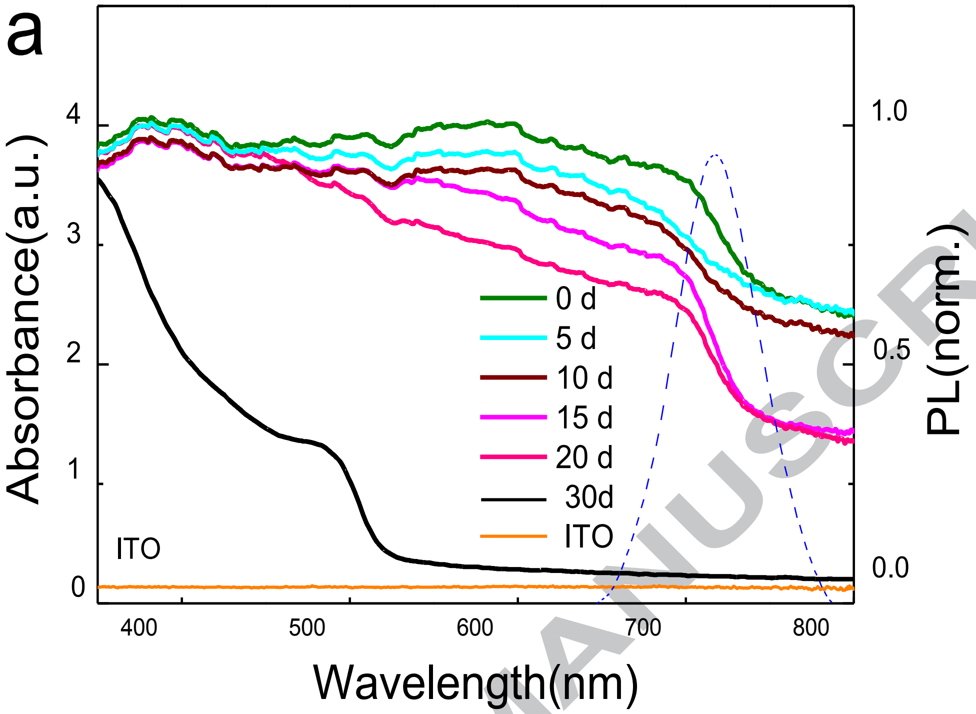


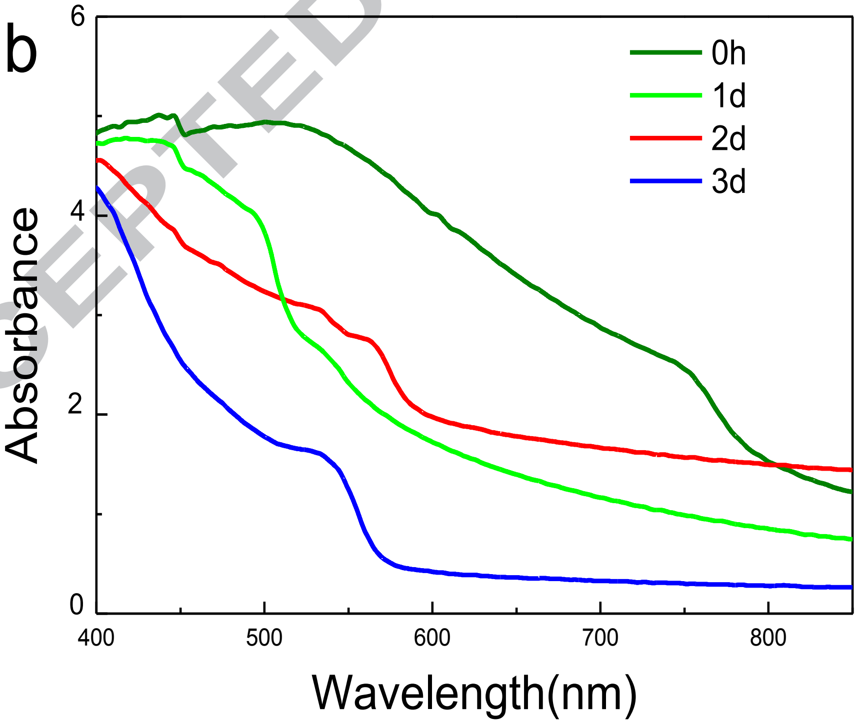


Figure 4 UV–vis absorption spectra for (a) (EDA)(MA)$_2$[Pb$_3$I$_{10}$] and (b) CH$_3$NH$_3$PbI$_3$ films in a 35 % RH environment at different time point.

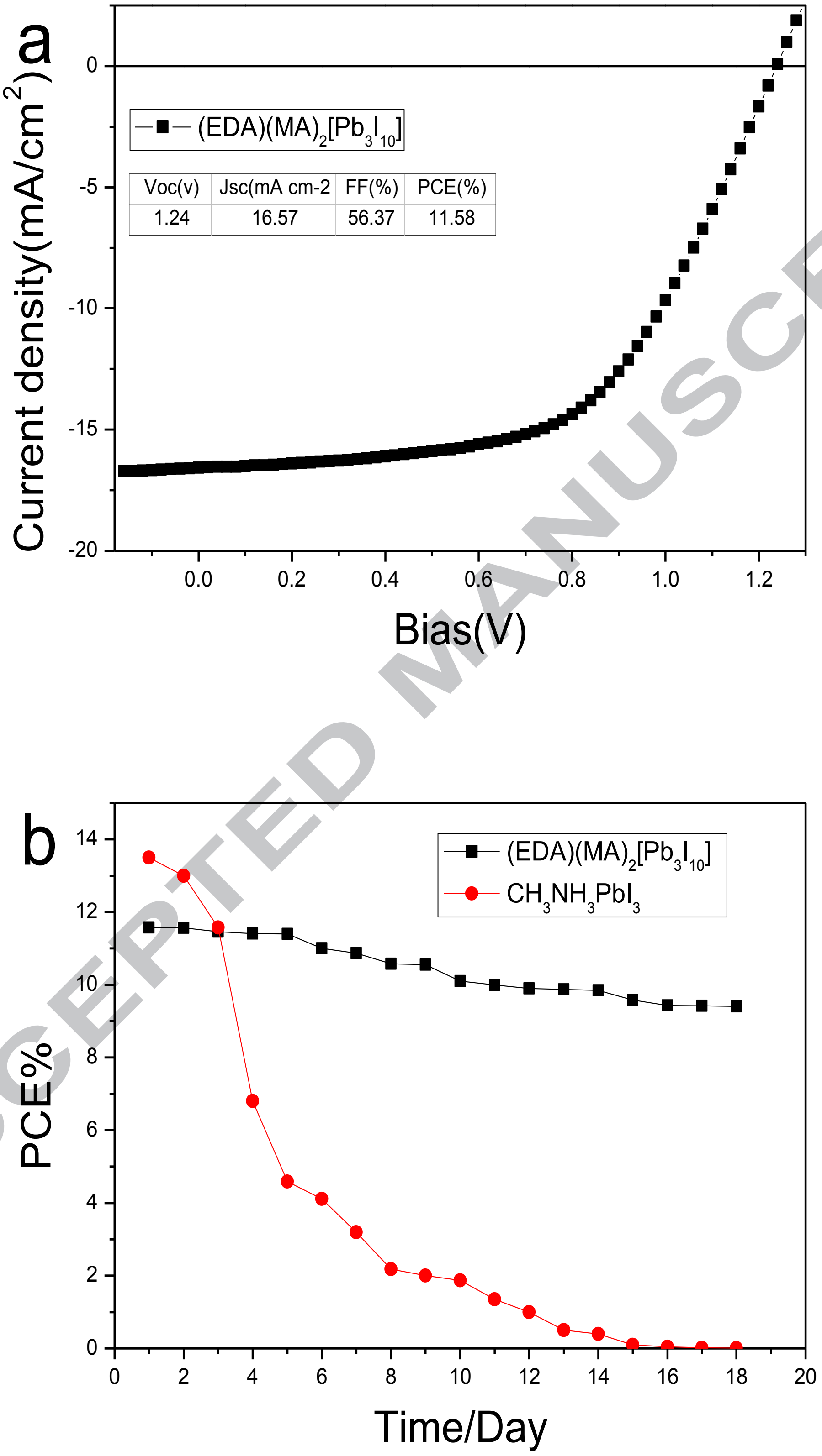
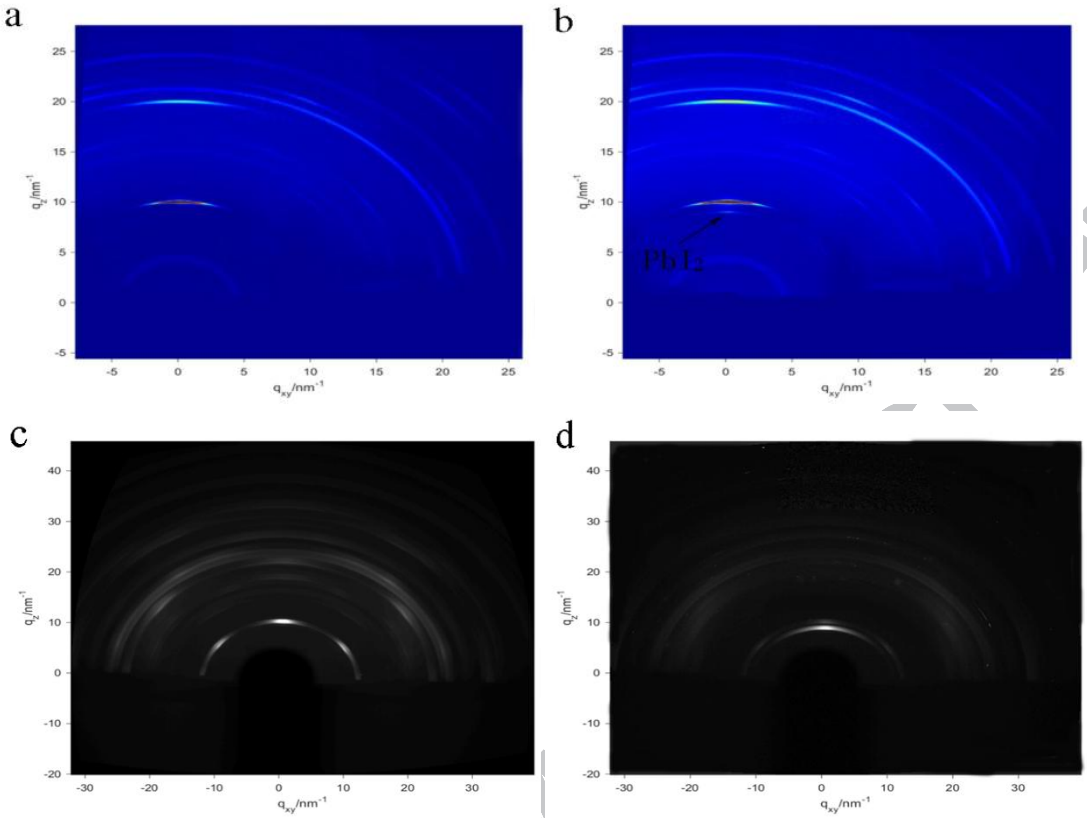


Figure 5 (a) J–V curves of solar cell with $(EDA)(MA)_2[Pb_3I_{10}]$ (b) Stability of the devices based on $(EDA)(MA)_2[Pb_3I_{10}]$ and $CH_3NH_3PbI_3$ in an ambient environment after encapsulation using UV-epoxy



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1. An EDA cation was first introduced into the perovskite lattice to synthesize a layered structure with high resistance to moisture degradation.
2. The effects of humidity and time on crystal structure of $(EDA)(MA)_2[Pb_3I_{10}]$ were analyzed by in situ grazing incidence X-ray diffraction(GIXRD).