Manipulation of perovskite film by bias-induced reversible lattice deformation toward tunable photoelectric performances

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Abstract
Organic lead halide perovskites have attracted extensive interest for potential use in next-generation photovoltaic devices due to the demonstrated high power conversion efficiency, low materials cost, and low fabrication cost. Besides, the electromechanical properties have also been explored in detail to expand the application potential. Here, we report the reversible photoelectric modulation (including photoresponse and photoresistance modulation, by near 6%) in methylammonium lead triiodide (MAPbI$_3$) film under an external electric bias (only 0.06 V/µm), which stems from the strain response induced by the competition of electrical biasing and light exposure. In addition, accompanied by the use of bias and light, the lattice is found to be deformed in MAPbI$_3$ film. This result does not only shed light on the lattice deformation from external factors but also highlights the dramatic electron/photon-lattice coupling in perovskite films.

1 | INTRODUCTION
In the past 10 years, we witnessed the explosion of solar cell research based on organic-inorganic hybrid perovskites (OIHPs), in particular methylammonium lead iodide (CH$_3$NH$_3$PbI$_3$, hereafter MAPbI$_3$). Especially, the solar cells based on that have achieved a certified power conversion efficiency of 25.5%, on the way approaching the theoretical limit of 31%. Concomitantly, due to extraordinary optoelectronic properties such as tunable bandgap in the visible range, long diffusion length, superb optical-absorption, small exciton binding energy, and even high ambipolar charge mobility, and so on, OIHPs have also been explored for lasers, light-emitting diodes, X-ray detectors, γ-ray detectors, and photodetectors.

A lot of work has been devoted to increase cell-efficiency and enhance photoelectric performances. Besides, classically physical methods are also developed gradually to explore the physical mechanism of perovskite. For instance, physical methods, such as electromagnetic fields or mechanical strain, have been performed on perovskite film (or bulk) to induce the change of significant...
2 | RESULT AND DISCUSSION

Firstly, we measure the photoresponsive performances of the film carried out on an Au/MAPbI3/glass structure under different bias voltages ($U_{Bias}$), as shown in Figure 1A. It is known that the reliable and rapid photoresponsive properties of perovskite films are intrinsic, so we characterize intuitively by an oscilloscope. All Au layers are acted as electrodes, including the lateral electrodes of film to apply regulated electric field and the electrodes on the surface of the film to test the photoresponsive performances. As shown in Figure 1B, there is a significant photoresponse of the film under the irradiation of laser (532 nm), which is visually observed by the changed voltage ($V$) signal in the oscilloscope. What's more, the photoresponse of film under $U_{Bias}$ (varying from 0 to 0.06 V $\mu$m$^{-1}$) is also obtained. It is found that the performance of MAPbI3 film remarkably enhances with increasing $U_{Bias}$. Then, we define this photoresponse as:

$$\Delta PR = \frac{|V_{light}(bias) - V_{light}(0)|}{V_{light}(0)} \times 100\%$$  (1)

where $V_{light}(bias)$ is $V$ under laser irradiation at a different bias. According to the result of bias-dependent photoresponse, the $\Delta PR$ is calculated in Figure 1C and exhibits an increase of almost 5.6% under 0.06 V $\mu$m$^{-1}$ of bias (Figure 1C). The relaxation times (the rise time, denoted as $\tau_{up}$, relates to switching on the laser; the decay time, denoted as $\tau_{down}$, relates to switching off the laser) of photoresponse under different bias also are characterized and fitted by the exponential function,$^{27}$ as shown in Figure 1D. It is
observed that the bias can effectively shorten the relative relaxation times, that is, the electric bias plays a prominent role in influencing the photoresponse behavior of perovskite film.

To explain the mechanism of the observed photoreponse modulation in perovskite film, given the discovery of a large electrostrictive response in MAPbI$_3$,[25] the lattice deformation of MAPbI$_3$ under $U_{\text{Bias}}$ brings strongly to our attention. Figure 2A presents in situ XRD patterns of MAPbI$_3$/glass under the electric bias. In Figure 2B, the (220) diffraction peak shifts toward higher angles with increasing bias voltage (about 0.003° under 0.06 V μm$^{-1}$). According to Bragg’s law and Poisson ratio,[28] the lattice deformation of MAPbI$_3$ film can be obtained evidently, which shows the contraction of crystals along the in-plane direction and the expansion in the perpendicular direction. Importantly, those directions of lattice deformation are consistent with the electrostrictive response discovered in MAPbI$_3$.[25] Also, the lattice change is around 0.01% under an applied electric field for only 0.06 V μm$^{-1}$, so does the reported electrostrictive response.[26] It is reported that the strain plays an indispensable role in influencing the electronic band structure of perovskites and the lattice deformation can give rise to the modulation of photoresistance for MAPbI$_3$ film.[26,29] Thus, we propose that the electrostriction causes the lattice deformation which can affect the photoresponse behavior of perovskite film.

In order to further investigate the relationship between the lattice deformation and the modulation of photoreponsive performances, we measure the temporal behavior of resistance ($R_{\text{light}}$) of MAPbI$_3$ film at a closed-loop bias (532 nm laser and 0–0.06 V μm$^{-1}$). The inset of Figure 3A shows the electrical measurement circuit. As shown in Figure 3A, the $R_{\text{light}}$ is highly sensitive to the electrical bias, and monotonically decreases with increasing bias voltage. Relative change of $R_{\text{light}}$, as $\Delta R/R_{\text{light}}$, is calculated using the below formula:

$$\Delta R/R_{\text{light}} = \frac{|R_{\text{light}}(\text{bias}) - R_{\text{light}}(0)|}{R_{\text{light}}(0)} \times 100\%$$  \hspace{1cm} (2)

where $R_{\text{light}}(\text{bias})$ is $R_{\text{light}}$ under the bias. To be noted, a V-shaped behavior corresponds to the incoherence of $\Delta R/R_{\text{light}}$ on bias polarity, as shown in Figure 3B, which also agrees with the strain change of MAPbI$_3$ film under different bias. Importantly, it further indicates the dominant role of the lattice deformation in the photoresistance modulation,[26] which is subjected to further analysis.

Furthermore, the bias-dependent $R_{\text{light}}$ of MAPbI$_3$ film is also measured under different irradiation powers in Figure 3C. According to that, we calculated the $\Delta R/R_{\text{light}}$ at different irradiation powers (Figure 3D). The inset of Figure 3D shows the power-dependent $\Delta R/R_{\text{light}}$ at 0.06 V μm$^{-1}$. It is found that $R_{\text{light}}$ of the film decreases with increasing irradiation power, stemming from the added photon injection. On the contrary, $\Delta R/R_{\text{light}}$ significantly decreases. Here, based on the analysis above, the photostrictive response can be taken into consideration. It is reported that when the laser shines on the MAPbI$_3$ crystal, a sudden change in the dimension would occur, namely, the laser-induced lattice deformation.[30] Importantly, for MAPbI$_3$, the direction of lattice deformation induced by the photostrictive response in the in-plane is contrary to the electrostrictive response.[25,36] Thus, we propose that the decrease of $\Delta R/R_{\text{light}}$ induced by the enhanced irradiation power, that is, the weakened photoreponse modulation, is attributed to the suppression of lattice deformation.

Naturally, structural distortion plays a key role in carrier localization.[31–34] The observed contraction of
FIGURE 3  A, Photoresistance ($R_{\text{light}}$) of MAPbI$_3$ film as a function of time under a closed-loop bias. The inset shows the schematic of photoresistance measurement. B, The calculated relative change of photoresistance ($\Delta R/R_{\text{light}}$) of film as a function of $U_{\text{Bias}}$. The black arrows show the scanning direction of the electric field. C, The bias-dependent $R_{\text{light}}$ under different irradiation powers. D, $\Delta R/R_{\text{light}}$ as a function of $U_{\text{Bias}}$ under different irradiation powers. The inset shows the power-dependent $\Delta R/R_{\text{light}}$ at 0.06 V/µm.

As a control experiment, we also prepared Cr-doped MAPbI$_3$ (MAPb$_{1-x}$Cr$_x$I$_3$, here $x = 0, 0.02, 0.06$) films and investigated their photoresistance-bias modulation. Firstly, we examine the structural evolution as a function of $x$ by using XRD. As shown in Figure 4A, the typical patterns of the tetragonal perovskite phases are noticed in all samples and the secondary or impure phases are absent. By enlarging the XRD patterns, it is found that the position is stable at 14.08° with increasing $x$, as shown in the inset of Figure 4A. Secondly, we also conduct the measurements of the $R_{\text{light}}$ at a closed-loop bias for Cr-doped perovskite films (Figure 4B) and find the bias-sensitive $R_{\text{light}}$, from which the relative change of $R_{\text{light}}$ of films is calculated, as shown in Figure 4C. We mainly focus on the difference between photoresistance modulation in the MAPbI$_3$ film and Cr-doped perovskite films. It is observed that the photoresistance modulation varies impressively with $x$. For MAPb$_{0.97}$Cr$_{0.02}$I$_3$ film, $R_{\text{light}}$ decreases with increasing bias, that is, the modulation behavior is similar but weaker to the observed in MAPbI$_3$ film. However, for MAPb$_{0.91}$Cr$_{0.03}$I$_3$ film, $R_{\text{light}}$ changes non-monotonically (decreases firstly and increases later) as a function of bias voltage. The above reveals that the capacity of photoelectric modulation in MAPbI$_3$ film is an inherent property (instead of measurement errors) and is closely related to lattice deformation induced by the coactions between electrical bias and light. Figure 4D shows the top-view SEM images, which shows the compact, and pinhole-free perovskite films and reveals the change of and morphology induced by the Cr-doped.

3 | CONCLUSION

In summary, the electrostrictive response has been observed in perovskite film, based on which we investigated a physical method of using electric bias that can impressively induce reversible lattice deformation in perovskite film toward significantly modulation photoelectric
properties. It is witnessed that the photoresponse and photoresistance are achieved a change of 6%. Importantly, that change, in concert with lattice deformation, can be recovered to its original value timely when removing the electric bias. Further analyses prove that the lattice deformation originates from the competitive effect of electric bias and light. In general, this work provides a new platform for not only manipulating the photoelectronic properties of perovskite films and exploring the physical properties of these materials but also giving light to the development of more methods.

4 | EXPERIMENTAL SECTION

4.1 | Perovskite film Preparation

Glass substrates were cleaned with detergent solution, deionized water, isopropanol, and absolute ethyl alcohol with 15 min of sonication for each step and finally transferred to argon-filled compact plasma sputtering coater for 40 min to increase hydrophilicity. Then, the substrates were transferred to an N₂-filled glovebox. Methylammonium iodide (CH₃NH₃I, MAI), lead acetate trihydrate (Pb(CH₃COO)₂·3H₂O, or PbAc₂·3H₂O) and chromium acetate (Cr(CH₃COO)₃ or CrAc₃) were purchased from Xi’an Polymer Light Technology Corp. Firstly, CrAc₃ is soluble in dimethylformamide. Moreover, a one-step method for preparing perovskite films can preserve Cr element in perovskite films. 0.6 mmol of MAI was dissolved in 0.2 mL of anhydrous N, N-dimethylformamide (DMF), and then added to 0.2 mmol mixture of PbAc₂·3H₂O and CrAc₃, depending on the desired concentration, thus obtaining precursor solution (MAPb₁₋ₓCrₓI₃ is 1 M). The perovskite films were prepared by spin-coating precursor solution at 6000 rpm on glass substrates and the films were annealed at 100 °C for 5 minutes. Au electrodes for the transport measurement were deposited on the surface and lateral of perovskite films using a sputtering coater.

4.2 | Measurements

X-ray diffraction (XRD) was performed using an X-ray diffractometer (XRD-7000, Shimadzu) with a Cu-Kα radiation source (λ = 1.5406 Å) at a step size of 0.02°. The photoelectric performances (including photoresponse and photoresistance) of samples were measured using a low-noise probe station, a waveform oscilloscope, a power source, and a current-voltage source (6487 Keithley multimeter). All the measurements were carried out with in-plane applied voltage.

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DATA AVAILABILITY STATEMENT
Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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