Supporting Information

Effect of mechanical force on thermal stability reinforcement for lead based perovskite materials

Dong Ding, a Henan Li, a,b,c Jieni Li, a Zibo Li, a Huizhen Yao, a Lai Liu, a Bing Bing Tian, a Chenliang Su, a,d Fuming Chen, e Yumeng Shi, a,d

a. International Collaborative Laboratory of 2D Materials for Optoelectronics Science and Technology of Ministry of Education, College of Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, China.
b. College of Electronic Science and Technology, Shenzhen University, Shenzhen 518060, China.
c. Shenzhen Key Laboratory of Flexible Memory Materials and Devices, College of Electronic Science and Technology, Shenzhen University, Shenzhen 518060, China.
d. Engineering Technology Research Center for 2D Material Information Function Devices and Systems of Guangdong Province, College of Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, China.
e. School of Physics and Telecommunication Engineering, South China Normal University, Guangzhou 510006, China.

E-mail: henan.li@szu.edu.cn
1. Experimental methods

1.1 Materials: PbX$_2$ including PbI$_2$ (99.9%), PbBr$_2$ (99.9%), PbCl$_2$ (99.9%), and AX including MAI (99.5%), MABr (99.5%), MACl (99.5%), FAI (99.5%), FABr (99.5%), FACl (99.5%), CsI (99.9%), CsBr (99.9%), CsCl (99.9%) were purchased from Xi'an Polymer Light Technology Corp. N,N-dimethylformamide (DMF, anhydrous, 99.8%) was purchased from Aladdin. ITO-coated glass substrates were purchased from South China Science & Technology Company Limited. All chemicals were used as received with no further purification.

1.2 Study of thermal decomposition inhibition: ITO-coated glass substrates were cleaned with deionized water, acetone, isopropanol for 15 min before being dried at 60 °C, followed by treating with oxygen plasma before use. Pristine MAPbX$_3$ (X=I, Br, Cl) materials were prepared by one-step spin-coating method. Firstly, we blended PbX$_2$ and CH$_3$NH$_3$X (MAX) in a 1:1 molar ratio in a precursor solution dissolved in N,N-dimethylformamide (DMF) with a concentration of 1 mM, and MAPbX$_3$ materials were spin-coated atop the ITO-coated glass substrates using the precursor solution under the conditions of 500 rpm for 2 s, followed by 4000 rpm for 30 s. The as-prepared MAPbX$_3$ materials were annealed at 100 °C for 30 min and then cooled to room temperature, these samples are denoted as pristine MAPbX$_3$ (Sample 1).

Secondly, pristine MAPbX$_3$ were further annealed at 150 °C for 1 hour with or without pressure using an inclosed stainless steel mould as shown in Figure S1 and S2, and then cooled to room temperature, the resulted samples are denoted as Sample 2 or Sample 3, respectively. The pressure was 5 MPa, and was provided by a hydraulic machine (YLT-HP-9, Kejing Star), which can provide both temperature and pressure at the same time.

1.3 Monitoring of mechanical force induced reverse reaction of MAPbX$_3$ (X = I, Br, Cl) The mixture of PbX$_2$ (0.6 mmol) and MAX (0.6 mmol) were ground in a mortar at room temperature. The synthesis was conducted in a glovebox under an argon atmosphere using the same grinding technique but different grinding time, and the resulted powders were characterized by XRD and UV-visible absorption measurements.

1.4 Study of roles of diverse organic and inorganic components of APbX$_3$ in the mechanical force induced reconstruction reaction route

The mixture of PbX$_2$ (0.6 mmol) and AX (0.6 mmol), where A=FA$^+$ or Cs$^+$, X= I$^-$ or Br$^-$ or Cl$^-$, were ground in a mortar at room temperature. The synthesis was conducted in a glovebox under an argon atmosphere using the same grinding technique but different grinding time, and the resulted powders were characterized by XRD and UV-visible absorption measurements.
1.5 Photodetector Device Fabrication: Ground MAPbI\textsubscript{3} powder of 0.1 g was put into a square hole in the middle of a mould as illustrated in Figure S11 (the mould was made by polymer film with thickness of 0.125 mm, the size of square hole was 5 mm × 5 mm), and then it was covered by another polymer film (thickness of 0.025 mm) and pressed into a thin sheet by a hydraulic machine (YLT-HP-9, Kejing Star) under a pressure of 10 MPa for 20 min. Au electrodes were fabricated using thermal evaporation method in a vacuum chamber (ZD-450, ReBorn).

1.6 Characterization: XRD patterns were measured by Rigaku D/MAX-2500 X-ray diffractometer equipped with a Cu K\textalpha X-ray (\( \lambda = 1.54186 \) Å) tube. UV-vis absorption spectroscopy was collected by a UV-vis-NIR spectrophotometer (Cary 5000, Agilent technologies). The SEM image was acquired using a field-emission scanning electron microscope (Supra 55 Sapphire, Zeiss). Optoelectronic properties measurements were made using an electrochemical workstation (CH Instruments, model CHI760E) under simulated sunlight illumination at 33-100 mW cm\textsuperscript{-2} from a 500 W Xe lamp (Solar-500, Beijing NBET Technology). Before the test, the light intensity was calibrated by a solar power meter (TES-132, TES).
Figure S1. Photographs of resulted samples and the stainless steel mould.

Figure S2. Enlarged photographs of resulted samples and the stainless steel mould.
Figure S3. Photographs (a) and SEM image (b) of pressed MAI/PbI₂.

We loaded a layer of PbI₂ powder into a metal cup and pressed it dense, then loaded a layer of MAI powder on it, and pressed these two layers of powders under pressure of 1 MPa for 10 min. Then, it was obvious to find a black layer, as shown in Figure S3a, Figure S3b also shown three distinct layers, these results confirmed that PbI₂ and MAI reacted and were converted into MAPbI₃.
Figure S4. Photoresponse characteristics of the devices of pristine MAPbI$_3$ film, further annealed at 150 °C for 1 hour with or without pressure (5 MPa): (a) and (c) are J-V curves in dark and under illumination at incident light density of 80 mW/cm$^2$; (b) and (d) show photoresponse of the devices under ON/OFF light switching at incident light density of 80 mW/cm$^2$ and bias voltages of 5 V.

We have fabricated photodetector devices using MAPbI$_3$ films, and then the as-prepared MAPbI$_3$ films were annealed at 150 °C for 1 hour with or without pressure (5 MPa), respectively. We further compared the optoelectronic properties of these samples to evaluate the efficiency of pressure on thermal stability reinforcement. As shown in Fig.S4 (a) and (b), the pristine MAPbI$_3$ film is in dark black colour. However, after annealing at 150 °C for 1 hour, the colour of MAPbI$_3$ film became yellowish. The linear J-V curve and photocurrent of the device under ON/OFF switching cycles of light illumination indicate that the optoelectronic performance appreciably decreases after further annealing. The photocurrent of the device decreases from 1.2 µA to 4.5 nA at a bias voltage of 5 V, which is approximately three orders of magnitude less than that of the pristine one. As shown in Fig.S4 (c) and (d), when the pristine MAPbI$_3$ film was annealed with pressure at 150 °C for 1 hour, the colour of
the sample remains dark black. More importantly, the photocurrent of the pressure-loaded
device is almost identical to that of pristine one, indicating that optoelectronic property of
MAPbI₃ film is well preserved. These results confirm the utility of pressure on thermal
stability reinforcement for perovskite materials in the context of photoelectric device
application.
Figure S5 Schematic representation of improved thermal stability of APbX₃.
Figure S6. XRD patterns and photographs taken from the resulted powders of (a) mixture of PbBr$_2$ and MABr, (b) PbBr$_2$ and MABr mixture after grinding for 5 min, (c) PbBr$_2$ and MABr mixture after grinding for 100 min, (d) PbBr$_2$, MABr and small quantity of dimethyl formamide (DMF) mixture after grinding for 5 min.
Figure S7. Standard XRD patterns of Cs$_4$PbBr$_6$ (JCPDS No. 73-2478), CsPbBr$_3$ (JCPDS No. 54-751), Cs$_4$PbCl$_6$ (JCPDS No. 76-1530) and CsPbCl$_3$ (JCPDS No. 18-366).
Figure S8. Photographs of original MAX, FAX, CsX, PbX₂ (MA=CH₃NH₃⁺, FA=HC(NH₂)₂⁺, X=I, Br, Cl).

Figure S9. Photographs of various perovskite powders produced by mechanical grinding method.
Figure S10. UV-visible absorption spectra of APbX$_3$ powders.
Figure S11. Illustration of photodetector device fabrication.

Figure S12. SEM image of mechanically pressed MAPbI$_3$ sheet for photo detector fabrication.

Figure S13. (a) The schematic illustration of the device structure and digital optical image of MAPbI$_3$ thin sheet compressed from MAPbI$_3$ powder after Au electrodes deposition (b) J-V curve in dark and under illumination at different incident light densities. (c) Photoresponse of the devices under ON/OFF switching at incident light density of 100 mW cm$^{-2}$ and bias voltages of 1 V, 3 V and 5 V. (d) Time-dependent photocurrent response at incident light
density of 100 mW cm\(^{-2}\) and bias voltages of 5 V, highlighting a rise time of \(\sim 8\) ms and a decay time of \(\sim 20\) ms.

As schematically illustrated in Figure S13 (a), a MAPbI\(_3\) based photodetector was fabricated by pressing the grinding-generated MAPbI\(_3\) powder into a thin sheet (details are in the Experimental methods). Au electrodes were deposited directly on the MAPbI\(_3\) thin sheet by vacuum thermal evaporation method. The channel length and width are 5 and 1.5 mm, respectively. As shown in Figure S12, SEM image indicates the obtained MAPbI\(_3\) thin sheet formed a closely compacted layer, facilitating the transport of photo-generated charge carriers. The linear J-V curve shows the Ohmic contact between Au and perovskite, giving maximum on/off ratio of \(\sim 100\). When incident light density is increased from 33 mW cm\(^{-2}\) to 100 mW cm\(^{-2}\), photocurrent of the device remarkably enlarged accordingly, which can be attributed to the enhanced photon density of the incident light. Figure S13 (c) shows the photo current of the device under ON/OFF switching cycles with light illumination. The photocurrent could approach \(5.38 \times 10^{-6}\) A at a bias voltage of 5 V. No obvious degradation was detected over 75 s, indicating the stable photoresponse of the materials prepared by mechanical force. Responsivity \((R)\) and detectivity \((D^*)\) are calculated as following formulas:

\[
R = \frac{(I_{\text{Light}} - I_{\text{Dark}})}{P}
\]

\[
D^* = \frac{R}{\sqrt{2(2qJ_d)}}
\]

where, \(I_{\text{Light}}\) and \(I_{\text{Dark}}\) are the photocurrent and dark current of the photodetector, respectively, and \(P\) is the incident light intensity.

The calculated responsivity and detectivity of our photodetector are 0.7 mA/W and \(3 \times 10^9\) Jones at bias of 5V, respectively. Notably, as shown in Figure S13 (d), the rise time \((t_r)\) and decay time \((t_d)\) of this device are lower than 8 ms and 20 ms, respectively.
Table 1. Effective ionic radii of different ions.

<table>
<thead>
<tr>
<th></th>
<th>Effective ionic radii (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA⁺</td>
<td>180</td>
</tr>
<tr>
<td>FA⁺</td>
<td>201</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>202</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>119</td>
</tr>
<tr>
<td>I⁻</td>
<td>220</td>
</tr>
<tr>
<td>Br⁻</td>
<td>182</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>167</td>
</tr>
</tbody>
</table>

Table 2. Calculated Goldschmidt’s tolerance factor (t) and Octahedral factor (µ) of different perovskites.

<table>
<thead>
<tr>
<th></th>
<th>Goldschmidt’s tolerance factor t</th>
<th>Octahedral factor µ</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPbI₃</td>
<td>0.83434</td>
<td>0.54</td>
</tr>
<tr>
<td>FAPbI₃</td>
<td>0.87606</td>
<td>0.54</td>
</tr>
<tr>
<td>CsPbI₃</td>
<td>0.88023</td>
<td>0.54</td>
</tr>
<tr>
<td>MAPbBr₃</td>
<td>0.85041</td>
<td>0.65</td>
</tr>
<tr>
<td>FAPbBr₃</td>
<td>0.89739</td>
<td>0.65</td>
</tr>
<tr>
<td>CsPbBr₃</td>
<td>0.90209</td>
<td>0.65</td>
</tr>
<tr>
<td>MAPbCl₃</td>
<td>0.85792</td>
<td>0.71</td>
</tr>
<tr>
<td>FAPbCl₃</td>
<td>0.90737</td>
<td>0.71</td>
</tr>
<tr>
<td>CsPbCl₃</td>
<td>0.91232</td>
<td>0.71</td>
</tr>
</tbody>
</table>