

LETTER

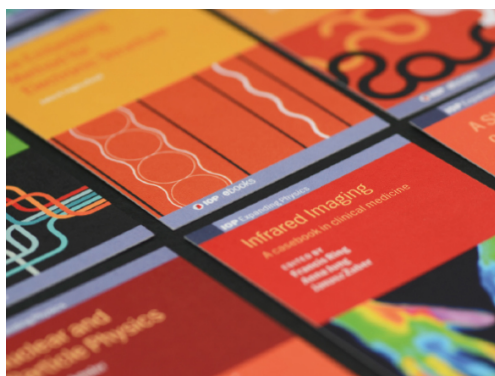
## Improved photoemission and stability of 2D organic-inorganic lead iodide perovskite films by polymer passivation

To cite this article: Mostafa M Abdelhamied *et al* 2020 *Nanotechnology* **31** 42LT01

View the [article online](#) for updates and enhancements.

### Recent citations

- [Synthesis and Optical Properties of PVA/PANI/Ag Nanocomposite films](#)  
M. M. Abdelhamied *et al*






**IOP | ebooks™**

Bringing together innovative digital publishing with leading authors from the global scientific community.

Start exploring the collection—download the first chapter of every title for free.

## Letter

# Improved photoemission and stability of 2D organic-inorganic lead iodide perovskite films by polymer passivation

Mostafa M Abdelhamied<sup>1,2,4</sup>, Yiling Song<sup>1,4</sup>, Weiwei Liu<sup>1</sup> , Xiaohong Li<sup>1</sup>, Hua Long<sup>1</sup> , Kai Wang<sup>1</sup> , Bing Wang<sup>1</sup> and Peixiang Lu<sup>1,3</sup>

<sup>1</sup> Wuhan National Laboratory for Optoelectronics and School of Physics, Huazhong University of Science and Technology, Wuhan 430074, People's Republic of China

<sup>2</sup> Radiation Physics Department, National Center for Radiation Research and Technology (NCRRT), Atomic Energy Authority (AEA), Cairo, Egypt

<sup>3</sup> Hubei Key Laboratory of Optical Information and Pattern Recognition, Wuhan Institute of Technology, Wuhan 430205, People's Republic of China

E-mail: [lwhust@hust.edu.cn](mailto:lwhust@hust.edu.cn)

Received 11 May 2020, revised 25 June 2020

Accepted for publication 30 June 2020

Published 24 July 2020



## Abstract

2D organic-inorganic lead iodide perovskites hold great promise for functional optoelectronic devices. However, their performances have been seriously limited by poor long-term stability in ambient environment. Here, we perform a systematic study for the stability improvement of a typical 2D organic-inorganic lead iodide perovskite (PEA)<sub>2</sub>PbI<sub>4</sub>. The degradation of the (PEA)<sub>2</sub>PbI<sub>4</sub> films can be attributed to the interaction with the humidity in environment, which leads to decomposition of the perovskite components. Then, we demonstrate that polymer passivation provides an effective approach for improving the crystal quality and stability of the (PEA)<sub>2</sub>PbI<sub>4</sub> films. Correspondingly, the photoemission of the polymer-passivated (PEA)<sub>2</sub>PbI<sub>4</sub> films has been enhanced due to the decreased trap states. More importantly, a hydrophobic polymer (Poly(4-Vinylpyridine), PVP) will protect the (PEA)<sub>2</sub>PbI<sub>4</sub> films from humidity in ambient environment, which can greatly improve the physical and chemical stability of the 2D perovskite films. As a result, the PVP-passivated (PEA)<sub>2</sub>PbI<sub>4</sub> films can produce a bright emission even after long-term (>15 d) exposure to ambient environment (25 °C, 80% RH) and continuous UV illumination. This work provides a convenient and effective approach for improving the long-term stability of 2D organic-inorganic lead iodide perovskites, which shows great promise for fabricating large-area and versatile optoelectronic devices.

Supplementary material for this article is available [online](#)

Keywords: 2D perovskites, photoemission, stability, polymer passivation, optoelectronic devices

(Some figures may appear in colour only in the online journal)

## 1. Introduction

Recently, organic-inorganic hybrid perovskites have shown great promise for functional optoelectronic devices including solar cells, light-emitting devices (LEDs), and optoelectronic

<sup>4</sup> Contributed equally to this work

detectors [1–7]. Organic-inorganic perovskites have a high band-edge absorption, a low defect density and a long carrier diffusion length [8–10]. The extraordinary optoelectronic characteristics and solution processability make it suitable for fabricating large-area and high-performance devices [11–13]. In particular, 2D organic-inorganic hybrid perovskites with a layered multi-quantum-well structure, have been demonstrated to possess a stronger quantum confinement [14–16] and a greater tenability [17–19]. Due to the more promising advantages compared to their 3D counterparts, 2D organic-inorganic hybrid perovskites have become a great candidate for next-generation optoelectronic devices [20–2627].

Although they have shown outstanding optical properties, organic-inorganic hybrid perovskites still suffer from poor stability caused by moisture, oxygen, interface defects and light illumination [28–33]. The instability will lead to a degradation of the perovskite in ambient environment, which has seriously limited the lifetime and performance of the optoelectronic devices based on perovskites. To overcome the shortage caused by the instability, great efforts have been made using surface passivation. For example, the stability of the 3D hybrid perovskite films could be enhanced by modifying the surface with crosslink groups [34, 35] and the surface defects can be passivated by using organic halide salt [36, 37]. More recently, potassium halide layers were demonstrated to be effective for passivating the perovskite interfaces and achieving high-stable photoluminescence (PL) emission [38]. However, for 2D organic-inorganic hybrid perovskites, the concerns about the stability still remains to be investigated in detail, which has great importance for fabricating high-performance functional devices.

In this work, we perform a systematic study on the degradation and stability improvement of a typical 2D organic-inorganic lead iodide perovskite (PEA)<sub>2</sub>PbI<sub>4</sub>. The degradation of the (PEA)<sub>2</sub>PbI<sub>4</sub> films can be attributed to a decomposition of the perovskite components, especially by interacting with the humidity and oxygen in the environment. Through surface passivation with a hydrophobic polymer, the surface traps of the (PEA)<sub>2</sub>PbI<sub>4</sub> films can be decreased. More importantly, the hydrophobic polymer will protect the hybrid perovskite from humidity in the environment and greatly improve the stability of the (PEA)<sub>2</sub>PbI<sub>4</sub> films. As a result, the polymer-passivated perovskite films can produce a bright emission even after long-term (>15 d) exposure to ambient environment and continuous UV illumination, which shows great promise for functional optoelectronic devices such as optoelectronic displays.

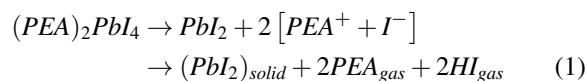
## 2. Result and discussion

(PEA)<sub>2</sub>PbI<sub>4</sub> films were prepared using a one-step spin-coating method (supporting information) [14]. After that, the films were systematically characterized by optical and morphological measurement. Figures 1(a) and (b) show the PL image and SEM image of the prepared (PEA)<sub>2</sub>PbI<sub>4</sub> film respectively. The PL image displays a bright and homogenous green emission, implying the good quality of the (PEA)<sub>2</sub>PbI<sub>4</sub> film. The SEM image shows that the 2D perovskite film consists of

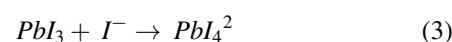
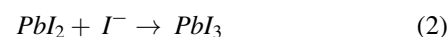
well-defined grains characterized as large crystals with average sizes between 5 ~ 15 μm. The XRD pattern in figure 1(c) displays well-defined diffraction patterns corresponding to the (00 *l*) series planes, and the narrow and sharp peaks imply a high quality of the perovskite film. Furthermore, figure 1(d) shows the absorption spectrum of an as-prepared (PEA)<sub>2</sub>PbI<sub>4</sub> film, which agrees well with the reported results [39, 40]. The absorption spectrum displays a narrow absorption peak located at ~ 517 nm, which corresponds to the intrinsic exciton absorption of (PEA)<sub>2</sub>PbI<sub>4</sub> [18].

To investigate the degradation of the (PEA)<sub>2</sub>PbI<sub>4</sub> films, the PL emission was monitored over time, as shown in figure 2(a). The samples were placed in ambient environment (25 °C, 80% RH), under continuous UV-light illumination. At first, the as-prepared (PEA)<sub>2</sub>PbI<sub>4</sub> film shows a bright green light, which is due to the exciton recombination of the 2D perovskite excited by high-energy photons. However, the green light becomes weaker over time and is completely quenched after about 4 d. To quantitatively characterize the degradation process, the PL intensity was extracted and plotted as a function of time, as shown in figure 2(b). We can observe that the PL intensity will decrease to 50% of the initial intensity after ~ 2 d, which shows direct evidence of the serious degradation of the 2D perovskite film.

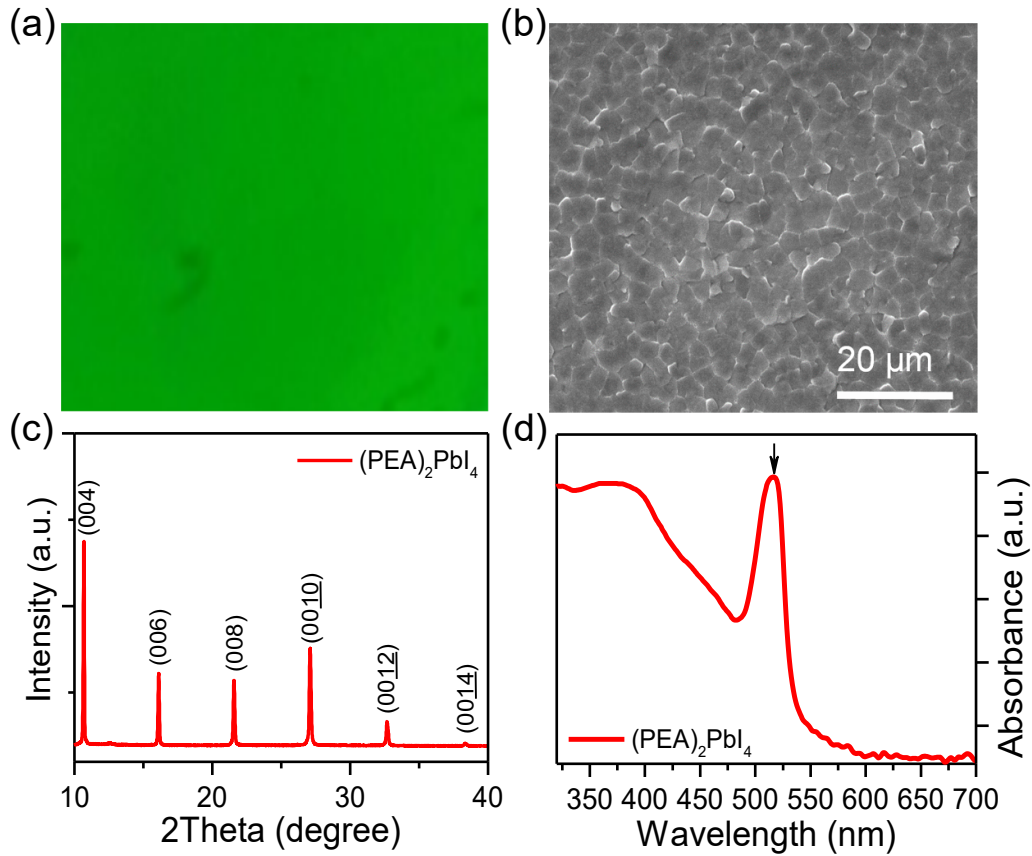
When exposed to ambient atmospheric conditions such as humidity, air and light illumination, the organic-inorganic hybrid perovskite will be degraded due to a series of reactions. To reveal the degradation mechanism of the (PEA)<sub>2</sub>PbI<sub>4</sub> films, the absorption spectrum of the film was measured over time. Figure 2(c) shows that the intensity of the exciton absorption peak largely decreases as time increases, and the absorption peak nearly disappears after 9 d (figure 2(d)), which is consistent with the PL measurement result. It is worth noting that, a new absorption peak located at ~ 410 nm appears in the absorption spectra, with the intensity growing gradually over time. The appearance of this absorption peak provides a strong evidence for the presence of PbI<sub>4</sub><sup>2-</sup> in the film during degradation [41]. The generation of PbI<sub>2</sub> in the organic-inorganic lead iodide perovskite films can be attributed to the following process [30]



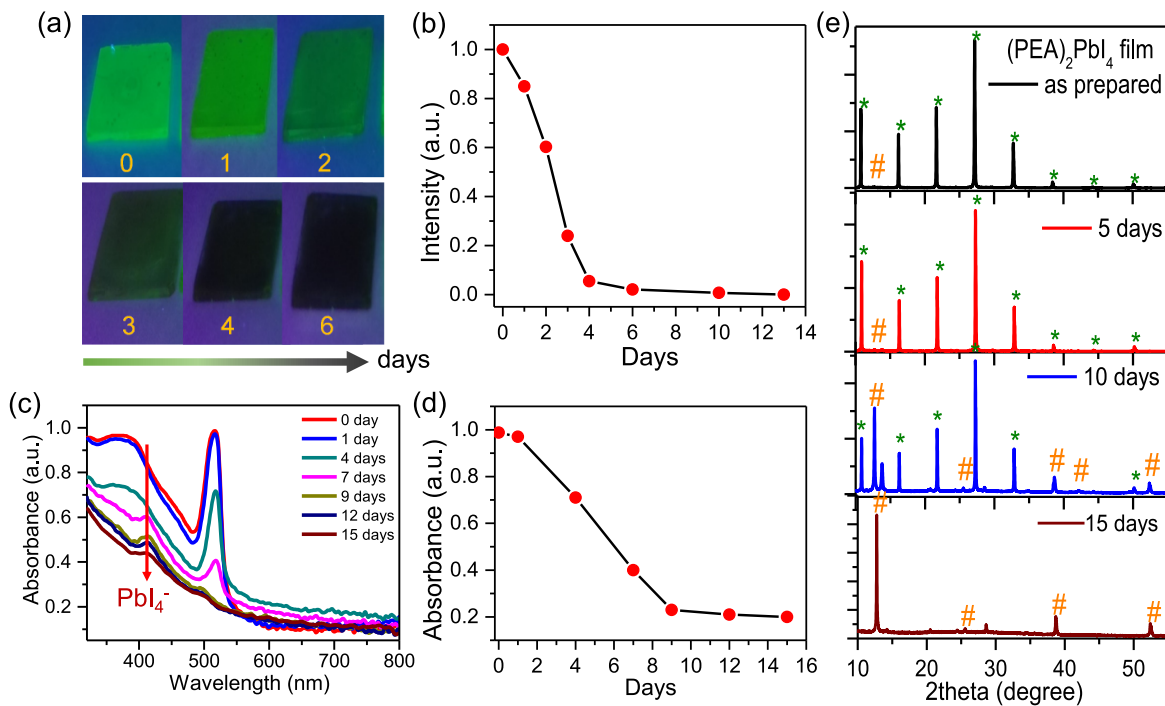
Moreover, tri- and tetra-iodoplumbate complexes will be produced due to the reaction between PbI<sub>2</sub> and I<sup>-</sup>, which can be expressed as



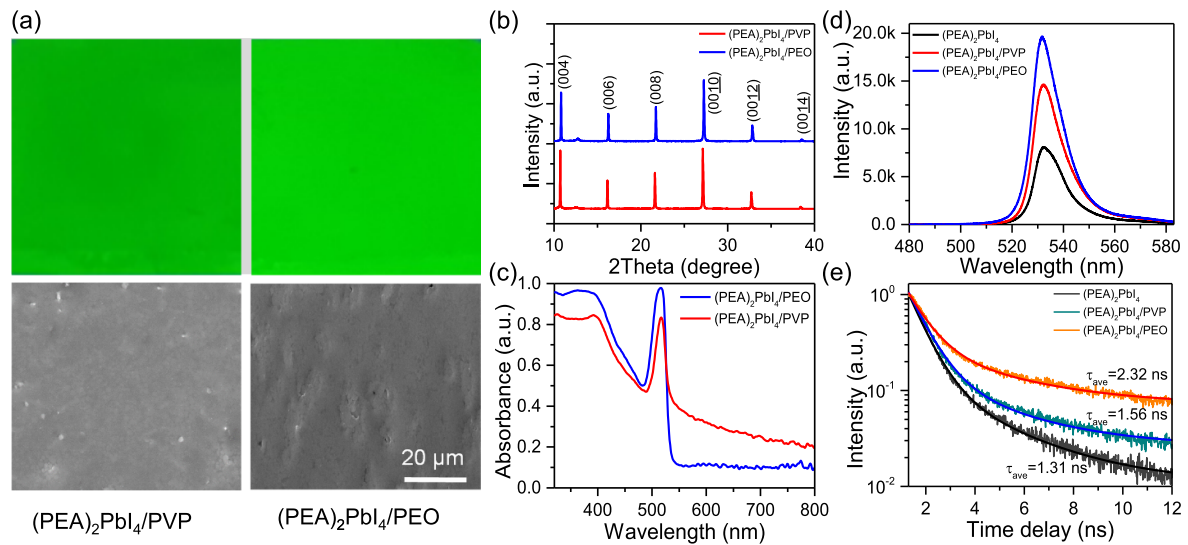
To further confirm the degradation process, XRD of the (PEA)<sub>2</sub>PbI<sub>4</sub> film was measured at various times, as shown in figure 2(e). After 5 d, the XRD peaks corresponding to the pristine (PEA)<sub>2</sub>PbI<sub>4</sub> shift slightly to larger diffraction angles, indicating that the perovskite grains have started to degrade



**Figure 1.** (a) PL image, (b) Top-view SEM image, (c) XRD pattern and (d) absorption spectrum of a pristine  $(\text{PEA})_2\text{PbI}_4$  film.



**Figure 2.** (a) Monitored PL images of a pristine  $(\text{PEA})_2\text{PbI}_4$  film over time. (b) Plot of corresponding PL intensities extracted from the PL images. (c) Monitored absorption spectrum of a pristine  $(\text{PEA})_2\text{PbI}_4$  film over time. (d) Plot of the exciton absorption peak intensity as a function of time. (e) XRD pattern of a pristine  $(\text{PEA})_2\text{PbI}_4$  film measured over time.



**Figure 3.** (a) PL images (top panel) and SEM images (bottom panel) of  $(\text{PEA})_2\text{PbI}_4/\text{PVP}$  and  $(\text{PEA})_2\text{PbI}_4/\text{PEO}$  films, respectively. (b) XRD patterns and (c) absorption spectra of the as-prepared  $(\text{PEA})_2\text{PbI}_4/\text{PVP}$  and  $(\text{PEA})_2\text{PbI}_4/\text{PEO}$  films respectively. (d) Measured PL spectra and (e) corresponding TRPL traces for the  $(\text{PEA})_2\text{PbI}_4$ ,  $(\text{PEA})_2\text{PbI}_4/\text{PVP}$  and  $(\text{PEA})_2\text{PbI}_4/\text{PEO}$  films respectively.

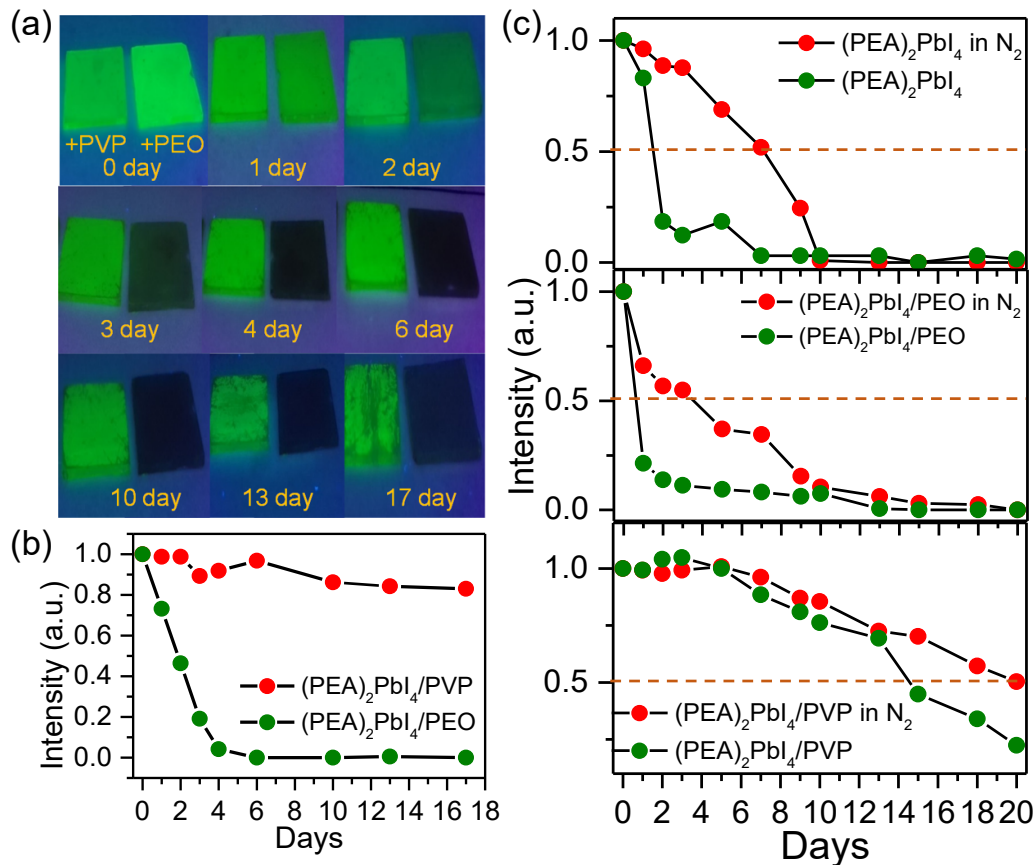
[30, 42]. Moreover, after 10-day exposure under UV light, a peak located at  $12.72^\circ$  increased significantly, with appearance of more new peaks located at  $25.55^\circ$ ,  $38.7^\circ$ ,  $44.3^\circ$  and  $52.34^\circ$  (labelled by #). Previous reports demonstrate that the new peaks can be attributed to the production of  $\text{PbI}_2$  in the perovskite film [43–45], which further confirm the degradation process expressed by equation (1). In particular, after 15 d, all of the XRD peaks corresponding to the pristine  $(\text{PEA})_2\text{PbI}_4$  disappear, suggesting complete degradation of the 2D perovskite film.

Surface passivation and encapsulation have shown great promise for effectively suppressing the degradation of the organic-inorganic perovskite in ambient environment [46–48]. To improve the stability of the  $(\text{PEA})_2\text{PbI}_4$  film, Poly(4-Vinylpyridine) (PVP) and Poly(ethylene oxide) (PEO) were used for encapsulation and surface passivation. The polymer solution was respectively coated on the perovskite films, forming the  $(\text{PEA})_2\text{PbI}_4/\text{PVP}$  and  $(\text{PEA})_2\text{PbI}_4/\text{PEO}$  composites. Figure 3(a) presents the PL images (top panel) and SEM images (bottom panel) of the  $(\text{PEA})_2\text{PbI}_4/\text{PVP}$  and  $(\text{PEA})_2\text{PbI}_4/\text{PEO}$  films respectively. The PL emission of the polymer encapsulated films has been increased compared with the intrinsic  $(\text{PEA})_2\text{PbI}_4$  film. After polymer deposition, the surface morphology of the films becomes smooth and exhibit no pinholes on the surface, especially by utilizing PVP layer, indicating a modification of the film quality. Moreover, polymer encapsulation can heal the defect states on the surface of the hybrid perovskite films, thus leading to a suppressed non-radiative recombination and an enhanced PL emission compared with the pristine perovskite film [12, 36, 49]. Figures 3(b) and (c) display the XRD patterns and absorption spectra of the  $(\text{PEA})_2\text{PbI}_4/\text{PVP}$  and  $(\text{PEA})_2\text{PbI}_4/\text{PEO}$  films respectively. The consistence of the XRD patterns and absorption spectra of the pristine  $(\text{PEA})_2\text{PbI}_4$  film and the polymer-coated ones suggests that the polymer passivation will not affect the crystal structure and bandgap of the  $(\text{PEA})_2\text{PbI}_4$  film.

**Table 1.** Fitted parameters for the PL decay traces of pristine  $(\text{PEA})_2\text{PbI}_4$  film,  $(\text{PEA})_2\text{PbI}_4/\text{PVP}$  film and  $(\text{PEA})_2\text{PbI}_4/\text{PEO}$  film. The average lifetime is calculated as  $\tau_{\text{ave}} = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$ .

	$(\text{PEA})_2\text{PbI}_4$	$(\text{PEA})_2\text{PbI}_4/\text{PVP}$	$(\text{PEA})_2\text{PbI}_4/\text{PEO}$
$A_1$	4019.5	3650.2	2688.3
$\tau_1/\text{ns}$	0.674	0.735	0.788
$A_2$	429.5	483.6	678.1
$\tau_2/\text{ns}$	2.767	3.12	3.63
$\tau_{\text{ave}}/\text{ns}$	1.31	1.56	2.32

To quantitatively characterize the photoemission performances of the  $(\text{PEA})_2\text{PbI}_4$  films encapsulated by PVP and PEO, PL spectra and lifetime were measured using a  $\mu$ -PL system. The samples were pumped with a femtosecond-pulsed Ti:sapphire laser (800 nm,  $\sim 8$  fs, 80 MHz), the infrared photons from which are beneficial for protecting the perovskite films from damage [18, 50–53]. Figure 3(d) displays the measured PL spectra of the  $(\text{PEA})_2\text{PbI}_4$  films, under a pumping power of 2 mW ( $\sim 2.6$  kW/cm<sup>2</sup>). As the photon energy of the femtosecond laser is smaller than the bandgap of  $(\text{PEA})_2\text{PbI}_4$ , the emission can be attributed to a two-photon absorption induced PL (figure S1, supporting information, available online at [stacks.iop.org/NANO/31/42LT01/mmedia](https://stacks.iop.org/NANO/31/42LT01/mmedia)). Notably, the PL intensity of the polymer-passivated  $(\text{PEA})_2\text{PbI}_4$  films is stronger than that of the pristine  $(\text{PEA})_2\text{PbI}_4$  film, which agrees well with the optical images in figure 3(a). Figure 3(e) presents the PL decay traces for the pristine  $(\text{PEA})_2\text{PbI}_4$  film,  $(\text{PEA})_2\text{PbI}_4/\text{PVP}$  film, and  $(\text{PEA})_2\text{PbI}_4/\text{PEO}$  film respectively. As reported, the PL emission of the 2D hybrid perovskites can originate from both the intrinsic exciton recombination and the trap states recombination. To reveal the two processes, all the decay traces can be fitted to a biexponential decay function  $I(t) = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2)$ . The fitted parameters



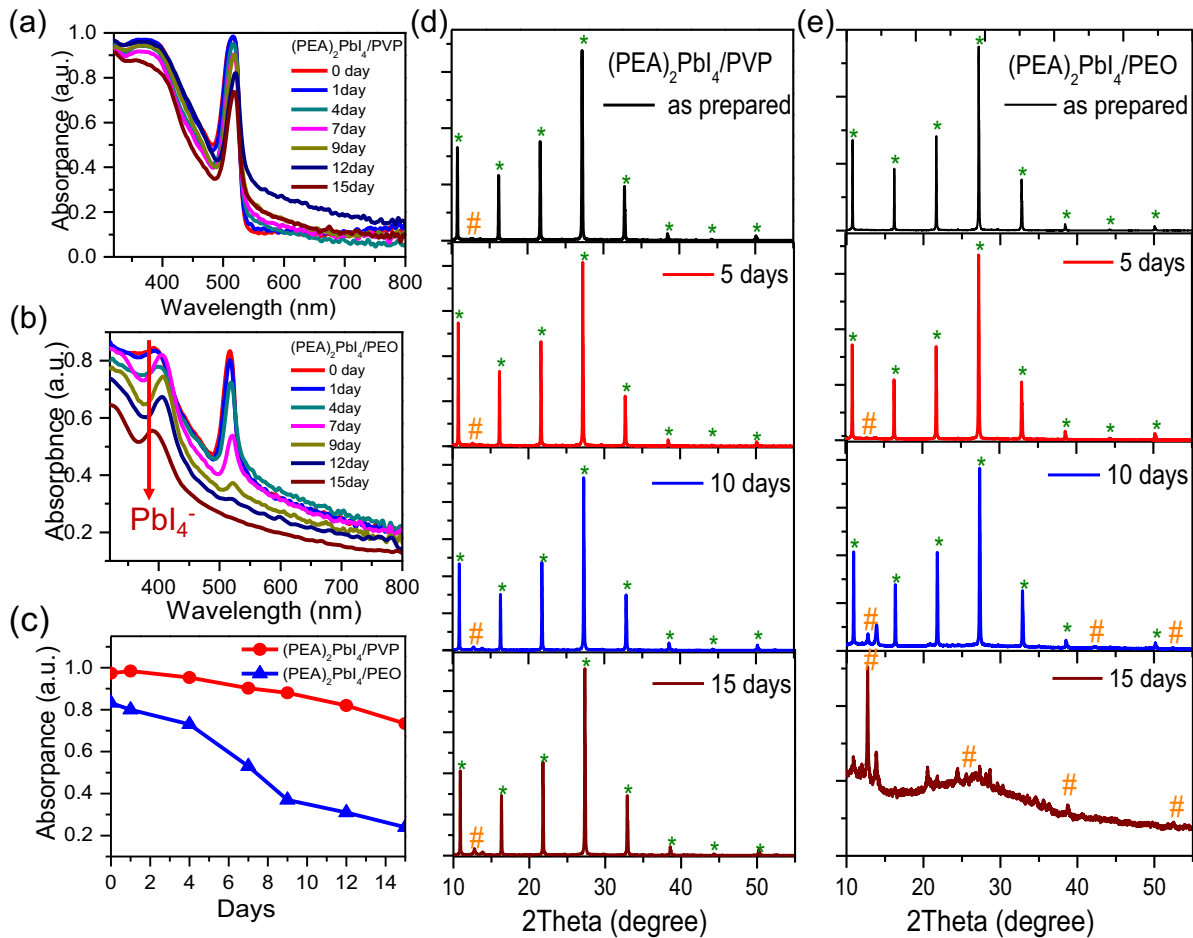
**Figure 4.** (a) Monitored PL images of the  $(\text{PEA})_2\text{PbI}_4/\text{PVP}$  and  $(\text{PEA})_2\text{PbI}_4/\text{PEO}$  films over time. (b) Plot of the extracted PL intensity of the  $(\text{PEA})_2\text{PbI}_4/\text{PVP}$  and  $(\text{PEA})_2\text{PbI}_4/\text{PEO}$  films as a function of time. (c) Plot of the extracted PL intensity of the  $(\text{PEA})_2\text{PbI}_4$ ,  $(\text{PEA})_2\text{PbI}_4/\text{PVP}$  and  $(\text{PEA})_2\text{PbI}_4/\text{PEO}$  films in ambient and in  $\text{N}_2$ , as a function of time.

are presented in table 1. In particular, the average lifetimes of the 2D perovskite films increase from 1.31 ns to 1.56 ns and 2.32 ns for  $(\text{PEA})_2\text{PbI}_4/\text{PVP}$  film and  $(\text{PEA})_2\text{PbI}_4/\text{PEO}$  film respectively. The increased PL lifetimes indicate that the nonradiative recombination is decreased in the polymer-encapsulated perovskite films, which is consistent with the PL enhancement and further demonstrates a suppression of the surface trap states [54, 55].

To investigate the effect of different polymer passivation on the stability of the  $(\text{PEA})_2\text{PbI}_4$  films, the samples were kept in ambient environment and exposed to continuous UV-light illumination. Figure 4(a) presents the PL images of the polymer-encapsulated films over time. One can observe that the PL emission of the  $(\text{PEA})_2\text{PbI}_4/\text{PEO}$  film quickly decreases, while the emission of the  $(\text{PEA})_2\text{PbI}_4/\text{PVP}$  film remains stable as time increases. To quantitatively characterize the PL variation, the intensity was extracted and plotted as a function of time, as shown in figure 4(b). For the  $(\text{PEA})_2\text{PbI}_4/\text{PEO}$  film, the PL intensity has been decreased to less than half of the initial intensity after 3 d, and it becomes completely quenched after 4 d, indicating that the samples have been damaged under UV light-irradiation. In contrast, the PL intensity of the  $(\text{PEA})_2\text{PbI}_4/\text{PVP}$  film has only decreased by 20% even after 17-days. Though the  $(\text{PEA})_2\text{PbI}_4/\text{PEO}$  film is isolated from air in the ambient environment, the degradation

property is the same as the intrinsic  $(\text{PEA})_2\text{PbI}_4$  film, demonstrating that humidity is the dominant factor which leads to the degradation of the organic-inorganic hybrid perovskites, especially exposed to continuous light illumination. In addition, we also monitored the degradation of the  $(\text{PEA})_2\text{PbI}_4$  films placed in a bag filled with dry  $\text{N}_2$  (figure 4(c) and figure S2, supporting information). The degradation of the pristine  $(\text{PEA})_2\text{PbI}_4$  film and  $(\text{PEA})_2\text{PbI}_4/\text{PEO}$  film has been greatly slowed down, demonstrating that the degradation can be dominantly attributed to the humidity in the ambient environment. As PEO is a hydrophilic polymer, it can absorb the water in the environment, further aggravating the degradation of the  $(\text{PEA})_2\text{PbI}_4$  film in humidity. In contrast, PVP is a hydrophobic polymer, which will prevent the  $(\text{PEA})_2\text{PbI}_4$  film from damage by the air and humidity from the environment. As a result, the PL emission from the  $(\text{PEA})_2\text{PbI}_4/\text{PVP}$  film remains nearly unchanged over time, and it is still quite bright even after a long time of 17 d. This result implies a great improvement of the stability of the 2D perovskite film for light illumination and air/humidity exposure by PVP polymer passivation.

To further demonstrate the stability improvement by PVP passivation, the absorption spectra of the pristine and polymer-encapsulated  $(\text{PEA})_2\text{PbI}_4$  films were measured over time, as shown in figures 5(a) and (b). The intensity at the exciton



**Figure 5.** Absorption spectra of the (a) (PEA)<sub>2</sub>PbI<sub>4</sub>/PVP film and (b) (PEA)<sub>2</sub>PbI<sub>4</sub>/PEO film, measured as a function of time. (c) Plot of the exciton absorption peak intensity of the (PEA)<sub>2</sub>PbI<sub>4</sub>/PVP and (PEA)<sub>2</sub>PbI<sub>4</sub>/PEO films. Measured XRD patterns of (d) (PEA)<sub>2</sub>PbI<sub>4</sub>/PVP film and (e) (PEA)<sub>2</sub>PbI<sub>4</sub>/PEO film, as a function of time.

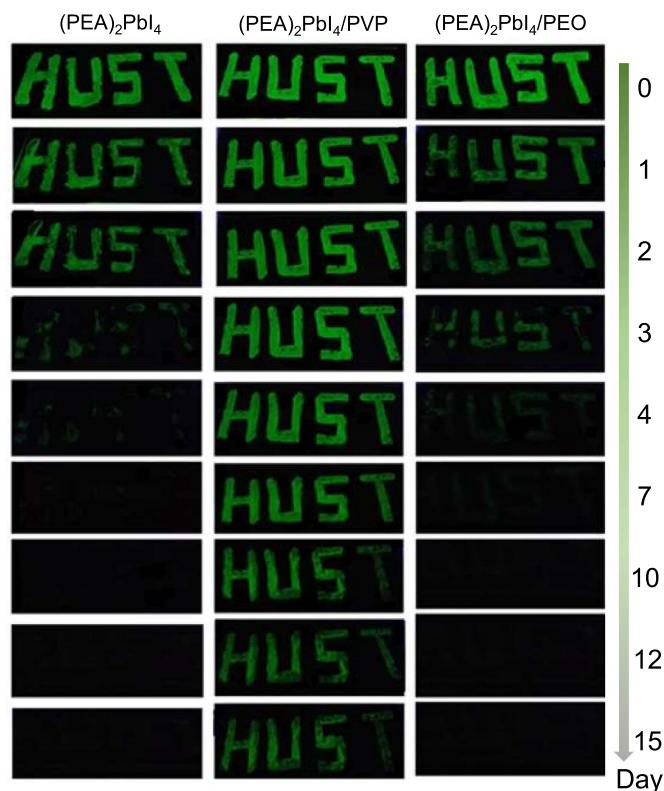
absorption peak was extracted and plotted in figure 5(c). Similar to the fluorescence result, the absorption spectrum of the (PEA)<sub>2</sub>PbI<sub>4</sub>/PVP film remains stable and the exciton absorption peak decreases to 80% of the initial intensity after 15 d. However, the absorption spectrum of the (PEA)<sub>2</sub>PbI<sub>4</sub>/PEO film exhibit a large decrease over a wide range, especially for the exciton absorption peak located at ~ 516.5 nm, which provides evidence for the degradation of the perovskite grains. In particular, the exciton absorption peak of the perovskite films disappear after 9 d, indicating that the perovskite has been completely damaged in the ambient environment. The stability of the (PEA)<sub>2</sub>PbI<sub>4</sub>/PVP film and (PEA)<sub>2</sub>PbI<sub>4</sub>/PEO film can be also revealed by the XRD measurement results, as shown in figures 5(d) and (e), respectively. Furthermore, a decreased PVP concentration exhibits a similar effect on the perovskite passivation, indicating an excellent performance of the PVP passivation layer (figure S3, supporting information).

Organic-inorganic lead iodide perovskite films are convenient for fabricating into large-area structures and patterns, which make them excellent candidates for practical applications in optoelectronic displays. To demonstrate the great promise of the polymer-passivated 2D perovskite films for functional applications, the (PEA)<sub>2</sub>PbI<sub>4</sub> solution was written

into a pattern spelling ‘HUST’, and then coated with polymer films. The PL emission from the films were monitored under continuous UV illumination, as shown in figure 6. One can observe that the pattern passivated by PVP can produce a clear and bright emission for a much longer time (>15 d) than the pristine and PEO-passivated (PEA)<sub>2</sub>PbI<sub>4</sub> films, indicating their great potential for light displays. Moreover, the (PEA)<sub>2</sub>PbI<sub>4</sub> film can be well protected by the PVP passivation layer, which is effective for increasing the physical and chemical stability of the perovskite films. Although some other materials such as 2D materials have also been proposed to suppress the degradation of hybrid perovskites due to their excellent stability [30, 56, 57], it is still difficult to efficiently cover the atomic-thin layers of the perovskite films. Therefore, the PVP-passivated 2D hybrid perovskite films shows great promise for large-area and versatile optoelectronic devices.

### 3. Conclusion

The stability issue of (PEA)<sub>2</sub>PbI<sub>4</sub> films was investigated by PL emission, absorption spectrum and XRD in ambient environment. The degradation mechanism of the (PEA)<sub>2</sub>PbI<sub>4</sub> films



**Figure 6.** Monitored PL images of ‘HUST’ patterns, composed of pristine  $(\text{PEA})_2\text{PbI}_4$  film,  $(\text{PEA})_2\text{PbI}_4/\text{PVP}$  film and  $(\text{PEA})_2\text{PbI}_4/\text{PEO}$  film respectively.

was revealed to be the interaction with humidity, which leads to decomposition of the perovskite components. More importantly, a hydrophobic polymer (PVP) encapsulation provides an effective approach for passivating surface traps and isolating the water from the environment. As a result, the PVP-passivated 2D organic-inorganic hybrid perovskite films can produce a bright emission even after long-term (>15 d) exposure to ambient environment and continuous UV illumination. This work provides a convenient and effective approach for improving the long-term stability of 2D organic-inorganic lead iodide perovskites, which shows great promise for fabricating large-area and versatile optoelectronic devices.

### Acknowledgments

This work was supported by the National Natural Science Foundation of China (Nos. 11804109, 11204097 and 11674117). We acknowledge the Analytical & Testing Center of Huazhong University of Science and Technology (HUST) for XRD measurements.

### ORCID iDs

Weiwei Liu  <https://orcid.org/0000-0001-9451-1968>  
 Hua Long  <https://orcid.org/0000-0002-7959-7828>  
 Kai Wang  <https://orcid.org/0000-0003-2122-1294>

### References

- [1] Yang W S, Noh J H, Jeon N J, Kim Y C, Ryu S, Seo J and Seok S I 2015 High-performance photovoltaic perovskite layers fabricated through intramolecular exchange *Science* **348** 1234–7
- [2] Zhao B *et al* 2018 High-efficiency perovskite–polymer bulk heterostructure light-emitting diodes *Nat. Photonics* **12** 783–9
- [3] Lin K B *et al* 2018 Perovskite light-emitting diodes with external quantum efficiency exceeding 20 per cent *Nature* **562** 245–8
- [4] Luo J J *et al* 2018 Efficient and stable emission of warm-white light from lead-free halide double perovskites *Nature* **563** 541–5
- [5] Turren-Cruz S H, Hagfeldt A and Saliba M 2018 Methylammonium-free, high-performance, and stable perovskite solar cells on a planar architecture *Science* **362** 449–53
- [6] Ji L, Hsu H Y, Lee J C, Bard A J and Yu E T 2018 High-performance photodetectors based on solution-processed epitaxial grown hybrid halide perovskites *Nano Lett.* **18** 994–1000
- [7] Yang Z, Zhang X, Yang W, Eperon G E and Ginger D S 2020 Tin–lead alloying for efficient and stable all-inorganic perovskite solar cells *Chem. Mater.* **32** 2782–94
- [8] Guo Z, Wan Y, Yang M J, Snaider J, Zhu K and Huang L B 2017 Long-range hot-carrier transport in hybrid perovskites visualized by ultrafast microscopy *Science* **356** 59–62
- [9] Pan D, Fu Y, Chen J, Czech K J, Wright J C and Jin S 2018 Visualization and studies of ion-diffusion kinetics in cesium lead bromide perovskite nanowires *Nano Lett.* **18** 1807–13
- [10] Chen T R *et al* 2017 Origin of long lifetime of band-edge charge carriers in organic-inorganic lead iodide perovskites *Proc. Natl Acad. Sci. USA* **114** 7519–24
- [11] Li X, Liu W, Song Y, Long H, Wang K, Wang B and Lu P 2020 Two-photon-pumped high-quality, single-mode vertical cavity lasing based on perovskite monocrystalline films *Nano Energy* **68** 104334
- [12] Zuo L J *et al* 2017 Polymer-modified halide perovskite films for efficient and stable planar heterojunction solar cells *Sci. Adv.* **3** e1700106
- [13] Cao Y *et al* 2018 Perovskite light-emitting diodes based on spontaneously formed submicrometre-scale structures *Nature* **562** 249–53
- [14] Liu W, Xing J, Zhao J, Wen X, Wang K, Lu P and Xiong Q 2017 Giant two-photon absorption and its saturation in 2D organic-inorganic perovskite *Adv. Opt. Mater.* **5** 1601045
- [15] Wei W J *et al* 2019 Regulating second-harmonic generation by van der Waals interactions in two-dimensional lead halide perovskite nanosheets *J. Am. Chem. Soc.* **141** 9134–9
- [16] Fang C, Wang H Z, Shen Z X, Shen H Z, Wang S, Ma J Q, Wang J, Luo H M and Li D H 2019 High-performance photodetectors based on lead-free 2D Ruddlesden-Popper perovskite/MoS<sub>2</sub> heterostructures *ACS. Appl. Mater. Inter.* **11** 8419–27
- [17] Blacon J C *et al* 2017 Extremely efficient internal exciton dissociation through edge states in layered 2D perovskites *Science* **355** 1288
- [18] Liu W, Li X, Song Y, Zhang C, Han X, Long H, Wang B, Wang K and Lu P 2018 Cooperative enhancement of two-photon-absorption-induced photoluminescence from a 2D perovskite-microsphere hybrid dielectric structure *Adv. Funct. Mater.* **28** 1707550
- [19] Hou L, Zhu Y, Zhu J and Li C 2019 Tuning optical properties of lead-free 2D tin-based perovskites with carbon chain spacers *J. Phys. Chem. C* **123** 31279–85
- [20] Tsai H H *et al* 2016 High-efficiency two-dimensional Ruddlesden-Popper perovskite solar cells *Nature* **536** 312–6



- [21] Yuan M J *et al* 2016 Perovskite energy funnels for efficient light-emitting diodes *Nat. Nanotechnol.* **11** 872–7
- [22] Liang D, Peng Y, Fu Y, Shearer M J, Zhang J, Zhai J, Zhang Y, Hamers R J, Andrew T L and Jin S 2016 Color-pure violet-light-emitting diodes based on layered lead halide perovskite nanoplates *ACS Nano* **10** 6879–904
- [23] Song Y L, Zhang C, Liu W W, Li X H, Long H, Wang K, Wang B and Lu P X 2018 High-efficiency energy transfer in perovskite heterostructures *Opt. Express* **26** 18448–56
- [24] Li J Z, Wang J, Ma J Q, Shen H Z, Li L, Duan X F and Li D H 2019 Self-trapped state enabled filterless narrowband photodetections in 2D layered perovskite single crystals *Nat. Commun.* **10** 806
- [25] Tremblay M-H *et al* 2019 (4NPEA)<sub>2</sub>PbI<sub>4</sub> (4NPEA = 4-Nitrophenylethylammonium): structural, NMR, and optical properties of a 3 × 3 corrugated 2D hybrid perovskite *J. Am. Chem. Soc.* **141** 4521–5
- [26] Tian X, Zhang Y, Zheng R, Wei D and Liu J 2020 Two-dimensional organic–inorganic hybrid Ruddlesden–Popper perovskite materials: preparation, enhanced stability, and applications in photodetection *Sustain. Energy Fuels* **4** 2087–113
- [27] Han T-H, Lee J-W, Choi Y J, Choi C, Tan S, Lee S-J, Zhao Y, Huang Y, Kim D and Yang Y 2020 Surface-2D/bulk-3D heterophased perovskite nanograins for long-term-stable light-emitting diodes *Adv. Mater.* **32** 1905674
- [28] Zhao J, Deng Y, Wei H, Zheng X, Yu Z, Shao Y, Shield J E and Huang J 2017 Strained hybrid perovskite thin films and their impact on the intrinsic stability of perovskite solar cells *Sci. Adv.* **3** eaao5616
- [29] Lin Y *et al* 2018 Excess charge-carrier induced instability of hybrid perovskites *Nat. Commun.* **9** 4981
- [30] Fang H H, Yang J, Tao S X, Adjokatse S, Kamminga M E, Ye J T, Blake G R, Even J and Loi M A 2018 Unravelling light-induced degradation of layered perovskite crystals and design of efficient encapsulation for improved photostability *Adv. Funct. Mater.* **28** 1800305
- [31] Song Y L, Liu W W, Fang C, Li D H and Lu P X 2019 Enhanced optoelectronic performance of 2D organic–inorganic hybrid perovskite through light-illumination *Opt. Express* **27** 30618–28
- [32] Bonabi Naghadeh S, Luo B, Abdelmageed G, Pu Y-C, Zhang C and Zhang J Z 2018 Photophysical properties and improved stability of organic–inorganic perovskite by surface passivation *J. Phys. Chem. C* **122** 15799–818
- [33] Song Y *et al* 2020 Photoinduced trap passivation for enhanced photoluminescence in 2D organic–inorganic hybrid perovskites *Adv. Opt. Mater.* **8** 1901695
- [34] Bai Y, Dong Q F, Shao Y C, Deng Y H, Wang Q, Shen L, Wang D, Wei W and Huang J S 2016 Enhancing stability and efficiency of perovskite solar cells with crosslinkable silane-functionalized and doped fullerene *Nat. Commun.* **7** 12806
- [35] Hu R, Zhang Y, Paek S, Gao -X-X, Li X A and Nazeeruddin M K 2020 Enhanced stability of  $\alpha$ -phase FAPbI<sub>3</sub> perovskite solar cells by insertion of 2D (PEA)<sub>2</sub>PbI<sub>4</sub> nanosheets *J. Mater. Chem. A* **8** 8058–64
- [36] Jiang Q, Zhao Y, Zhang X, Yang X, Chen Y, Chu Z, Ye Q, Li X, Yin Z and You J 2019 Surface passivation of perovskite film for efficient solar cells *Nat. Photonics* **13** 460–6
- [37] Alharbi E A *et al* 2019 Atomic-level passivation mechanism of ammonium salts enabling highly efficient perovskite solar cells *Nat. Commun.* **10** 3008
- [38] Abdi-Jalebi M *et al* 2018 Maximizing and stabilizing luminescence from halide perovskites with potassium passivation *Nature* **555** 497–501
- [39] Zhang S J *et al* 2010 Preparations and characterizations of luminescent two dimensional organic–inorganic perovskite semiconductors *Materials* **3** 3385–406
- [40] Ishihara T, Takahashi J and Goto T 1990 Optical-properties due to electronic-transitions in 2-dimensional semiconductors (CNH<sub>2n</sub> + 1NH<sub>3</sub>)<sub>2</sub>PbI<sub>4</sub> *Phys. Rev. B* **42** 11099–107
- [41] Stampelcoskie K G, Manser J S and Kamat P V 2015 Dual nature of the excited state in organic–inorganic lead halide perovskites *Energ. Environ. Sci.* **8** 208–15
- [42] Xiong H, DeLuca G, Rui Y, Zhang B, Li Y, Zhang Q, Wang H and Reichmanis E 2018 Modifying perovskite films with polyvinylpyrrolidone for ambient-air-stable highly bendable solar cells *ACS. Appl. Mater. Inter.* **10** 35385–94
- [43] Bai S *et al* 2019 Planar perovskite solar cells with long-term stability using ionic liquid additives *Nature* **571** 245–50
- [44] Hwang I, Jeong I, Lee J, Ko M J and Yong K 2015 Enhancing stability of perovskite solar cells to moisture by the facile hydrophobic passivation *ACS. Appl. Mater. Inter.* **7** 17330–6
- [45] Han T H *et al* 2019 Perovskite-polymer composite cross-linker approach for highly-stable and efficient perovskite solar cells *Nat. Commun.* **10** 520
- [46] Raja S N, Bekenstein Y, Koc M A, Fischer S, Zhang D, Lin L, Ritchie R O, Yang P and Alivisatos A P 2016 Encapsulation of perovskite nanocrystals into macroscale polymer matrices: enhanced stability and polarization *ACS. Appl. Mater. Inter.* **8** 35523–33
- [47] Crespo-Quesada M, Pazos-Outón L M, Warnan J, Kuehnel M F, Friend R H and Reisner E 2016 Metal-encapsulated organolead halide perovskite photocathode for solar-driven hydrogen evolution in water *Nat. Commun.* **7** 12555
- [48] Wei Y, Deng X, Xie Z, Cai X, Liang S, Ma P A, Hou Z, Cheng Z and Lin J 2017 Enhancing the stability of perovskite quantum dots by encapsulation in crosslinked polystyrene beads via a swelling–shrinking strategy toward superior water resistance *Adv. Funct. Mater.* **27** 1703535
- [49] Kim M, Motti S G, Sorrentino R and Petrozza A 2018 Enhanced solar cell stability by hygroscopic polymer passivation of metal halide perovskite thin film *Energ. Environ. Sci.* **11** 2609–19
- [50] Kinyua D M, Long H, Xing X Y, Njoroge S, Wang K, Wang B and Lu P X 2019 Gigahertz acoustic vibrations of Ga-doped ZnO nanoparticle array *Nanotechnology* **30** 305201
- [51] Li J P, Zhang Q B, Li L, Zhu X S, Huang T F, Lan P F and Lu P X 2019 Orientation dependence of high-order harmonic generation in nanowire *Phys. Rev. A* **99** 033421
- [52] Zhao Y, Zhou Y M, Liang J T, Zeng Z X, Ke Q H, Liu Y L, Li M and Lu P X 2019 Frustrated tunneling ionization in the elliptically polarized strong laser fields *Opt. Express* **27** 21689–701
- [53] Han X, Wang K, Long H, Hu H, Chen J, Wang B and Lu P 2016 Highly sensitive detection of the lattice distortion in single bent ZnO nanowires by second-harmonic generation microscopy *ACS Photonics* **3** 1308–14
- [54] Wang Y *et al* 2016 Ultrastable, highly luminescent organic–inorganic perovskite-polymer composite films *Adv. Mater.* **28** 10710–7
- [55] Bi D Q, Yi C Y, Luo J S, Decoppet J D, Zhang F, Zakeeruddin S M, Li X, Hagfeldt A and Gratzel M 2016 Polymer-templated nucleation and crystal growth of perovskite films for solar cells with efficiency greater than 21% *Nat. Energy* **1** 16142
- [56] Li X, Liu W, Song Y, Zhang C, Long H, Wang K, Wang B and Lu P 2019 Enhancement of the second harmonic generation from WS<sub>2</sub> monolayers by cooperating with dielectric microspheres *Adv. Opt. Mater.* **7** 1801270
- [57] Fan Z *et al* 2017 Layer-by-layer degradation of methylammonium lead tri-iodide perovskite microplates *Joule* **1** 548–62