

# Long-term Stable 2D Dion-Jacobson Phase Perovskite Photodiode with Low Dark Current and High On/off Ratio<sup>①</sup>

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**ABSTRACT** A two-dimensional (2D) organic-inorganic hybrid perovskite (OIHP) material is considered as a promising candidate for a long-term stable photodetector owing to its outstanding phase and environmental stability. Herein, we demonstrate a perovskite photodiode based on the DJ phase 2D perovskite (PDA)(MA)<sub>n-1</sub>Pb<sub>n</sub>I<sub>3n+1</sub> (where PDA is 1,3-propylenediamine, MA is methylamine, nominal  $n = 4$ ). The best-performance device exhibits a high detectivity of  $4.57 \times 10^{11}$  Jones, a responsivity of  $0.25 \text{ A} \cdot \text{W}^{-1}$  at 480 nm, a low dark current density of  $9.60 \times 10^{-4} \text{ mA} \cdot \text{cm}^{-2}$ , and a remarkable on/off ratio of  $3.10 \times 10^5$ . The unencapsulated device can maintain 95% of the initial photocurrent density after 90 days under an ambient atmosphere with relative humidity (RH) of 65%, demonstrating its improved stability than the 3D counterpart. The excellent stability of the photodiode based on 2D perovskite promises its bright commercial application future.

**Keywords:** two-dimensional perovskite, Dion-Jacobson, photodiode, on/off ratio, stability;

**DOI:** 10.14102/j.cnki.0254-5861.2011-3200

## 1 INTRODUCTION

As a kind of photoelectronic devices to convert optical signals into electrical signals, photodetectors are widely used in aerospace communication, environmental monitor, biological sensor, and other fields<sup>[1-5]</sup>. At present, commercial photodetectors are mostly based on III-V inorganic semiconductors such as silicon (Si) and germanium (Ge), but they have the drawbacks of high cost and complicated fabrication process<sup>[6-9]</sup>. Therefore, it is urgent to fabricate photodetectors with low cost and simple preparation process. In recent years, perovskite materials have attracted increasing attention due to their excellent merits including high carrier mobility, adjustable bandgap, long charge diffusion length, and simple fabrication process<sup>[10-13]</sup>. As a typical organic-inorganic hybrid perovskite (OIHP), CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> (MAPbI<sub>3</sub>) has been used for various practical applications such as solar cells, light-emitting diodes (LED), photodetectors, lasers, etc.<sup>[14-18]</sup>. However, the poor moisture

and heat stability is still a problem that needs to be solved. Recently, two-dimensional (2D) OIHP materials, which are fabricated by adding a long chain or large volume organic ammonium salt to the perovskite components<sup>[19, 20]</sup>, are emerging due to their great potential to solve the stability issue of the conventional three-dimensional (3D) perovskite materials.

The 2D OIHP material was first used to improve the performance of solar cells. Smith et al. used (PEA)<sub>2</sub>(MA)<sub>2</sub>-Pb<sub>3</sub>I<sub>10</sub> (where PEA<sup>+</sup> is phenylethylammonium) as the active layer to fabricate solar cells with improved stability<sup>[21]</sup>. Some other organic ammonium salts have also been used to prepare 2D OIHP, such as 1,3-propylenediamine (PDA)<sup>[19]</sup>, butylamine (BA)<sup>[22]</sup>, and so on. The encouraging results of solar cells based on 2D perovskites inspire researchers to further explore other applications of the 2D perovskites. For example, Han et al. fabricated highly oriented thin films with a new 2D perovskite (PA)<sub>2</sub>(FA)Pb<sub>2</sub>I<sub>7</sub> (where PA is *n*-pentylaminium and FA is formamidine) for photodetectors,

Received 31 March 2021; accepted 26 May 2021

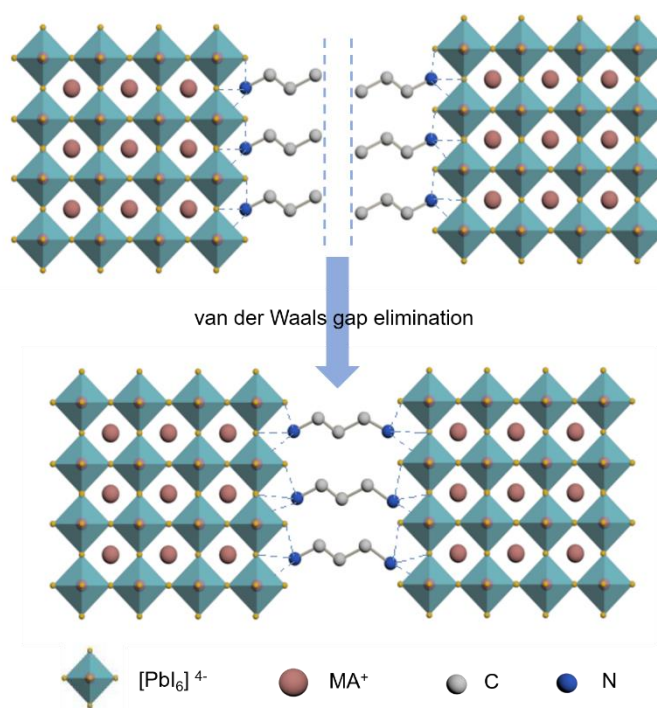
① Supported by the National Natural Science Foundation of China (No. U1605241), the Fujian Science & Technology Innovation Laboratory for Optoelectronic Information of China (No. 2021ZR116) and the Natural Science Foundation of Fujian Province for Distinguished Young Scholars (No. 2019J06023)

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which realized an ultrafast response time of 2.54 ns as well as a high responsivity of  $1.73 \times 10^{14}$  Jones<sup>[23]</sup>. Tsai *et al.* used a 2D perovskite  $(\text{BA})_2(\text{MA})_2\text{Pb}_3\text{I}_{10}$  for X-ray photodiodes that can work at a very low external bias<sup>[24]</sup>. Lim *et al.* developed a photodiode based on 2D perovskite by incorporating PEAI into  $\text{MAPbI}_3$ . The current density of the 2D perovskite photodiode maintained 76% of the initial current density after 80 days in the ambient condition, compared to 15% for the control sample of 3D perovskite photodiode<sup>[25]</sup>.

According to the types of organic amines used in the 2D perovskite, 2D perovskite can be divided into Ruddlesden-Popper (RP) and Dion-Jacobson (DJ) phases, which are prepared by using monoamine and diamine, respectively<sup>[26]</sup>. The RP phase 2D perovskite has a general formula of  $(\text{RNH}_3)_2\text{A}_{n-1}\text{M}_n\text{X}_{3n+1}$ , in which the monoammonium cations only interact with inorganic perovskite layers at one side, and van der Waals gap exists between the adjacent

cations. In the DJ phase 2D perovskite with a formula of  $(\text{NH}_3\text{RNH}_3)\text{A}_{n-1}\text{M}_n\text{X}_{3n+1}$ , hydrogen bonds are formed between the amino group and the inorganic component at both ends. Compared with the RP phase 2D perovskites, the DJ ones can possess better stability owing to the elimination of the van der Waals gap (see illustration in Fig. 1)<sup>[19, 27]</sup>. So far, there are only a few reports about the DJ phase perovskites for photodetectors<sup>[28, 29]</sup>. And, in the reports, a photoconductor device configuration was adopted for the DJ phase 2D perovskite photodetectors, which usually needs relatively high operating voltages. Meanwhile, they suffer from low on/off ratios ( $< 10^3$ ) which limit their further applications. In contrast, photodiode-type photodetectors can work at zero bias and exhibit high on/off ratios owing to the rather low dark currents although their EQEs are normally less than 1. To the best of our knowledge, DJ phase 2D perovskites have never been used for fabricating the photodiode-type photodetectors until now.



**Fig. 1.** Schematic illustration of RP and DJ phase 2D perovskites

Herein, we fabricated a high-performance stable photodetector based on a DJ phase 2D perovskite derived from 1,3-propyleneamine (PDA). A high-quality film of  $(\text{PDA})(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$  (nominal  $n = 4$ ) was prepared by one-step method. The resulting photodiodes exhibit lower dark current and better stability than the 3D reference devices. The device based on DJ phase 2D perovskite

exhibits a responsivity of  $0.25 \text{ A}\cdot\text{W}^{-1}$  and a high detectivity of  $4.57 \times 10^{11}$  Jones at 480 nm. In addition, the device has a dark current density as low as  $9.60 \times 10^{-4} \text{ mA}\cdot\text{cm}^{-2}$  and a maximum on/off ratio of  $3.10 \times 10^5$ , which are remarkable in the 2D perovskite photodiodes. Furthermore, the devices based on the DJ phase 2D perovskite layer without encapsulation can maintain 95% of the initial photocurrent

after storage for 90 days in the air with a relative humidity (RH) of 65%, while the conventional 3D perovskite photodiodes can only maintain 35% of the initial photocurrent after the same storage time.

## 2 EXPERIMENTAL

### 2.1 Materials

1,3-Propylenediamine and hydroiodic acid were purchased from Aladdin. The SnO<sub>2</sub> colloid precursor (Tin (IV) oxide, 15% in H<sub>2</sub>O colloidal dispersion) was purchased from Alfa Aesar. Lead iodide (PbI<sub>2</sub>) and methylammonium iodide (MAI) were purchased from Xi'an Polymer Technology Corp.. Dimethylformamide (DMF), dimethylsulfoxide (DMSO),  $\gamma$ -butyrolactone (GBL), and chlorobenzene (CB) were purchased from Sigma-Aldrich. 2,2',7,7'-Tetrakis[*N,N*-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (Spiro-OMeTAD) was purchased from Shenzhen Feiming Science and Technology Co., Ltd.

### 2.2 Synthesis of (PDA)I<sub>2</sub>

1,3-Propylenediamine iodide ((PDA)I<sub>2</sub>) was prepared by adding dropwise hydroiodic acid (3.40 mL, 30 mmol) to a solution of 1,3-propylenediamine (0.74 g, 10 mmol) in ethanol at 0 °C and stirring for 2 h<sup>[19]</sup>. The white precipitate of the diammonium iodide was recovered by evaporating the solvent at 55 °C using a rotary evaporator. The precipitate was washed three times with ether and dried overnight in an oven at 60 °C under reduced pressure to obtain a white powder (1.70 g, 85% yield).

### 2.3 Preparation of 2D perovskite film

The 2D perovskite PDA(MA)<sub>3</sub>Pb<sub>4</sub>I<sub>13</sub> precursor solutions (the concentration of Pb<sup>2+</sup> is 0.8 M) were prepared by dissolving a stoichiometric ratio of 4:3:1 of PbI<sub>2</sub>, MAI, and (PDA)I<sub>2</sub> in the mixed solution of GBL:DMSO (7:3, volume ratio), and then stirred at 65 °C before use. The prepared solutions were filtered by PTFE syringe filter (0.2  $\mu$ m) and coated onto the substrate with a consecutive spin-coating process at 6000 rpm for 35 s. Before the end of 15 s, 100  $\mu$ L of chlorobenzene was dropped onto the perovskite film for better crystallization, followed by annealing at 120 °C for 10 min.

### 2.4 Fabrication of devices

ITO glass substrates were cleaned *via* sequential ultrasonic treatments with acetone, isopropyl alcohol, and deionized water for 30 min, respectively. Then, they are dried in the oven at 75 °C. Before deposition of the SnO<sub>2</sub>

electron transport layer (ETL), the ITO substrates were pretreated by UV-O<sub>3</sub> for 15 min. And the SnO<sub>2</sub> colloid solution with a concentration of 7.5 wt% was spin-coated on the ITO at 3000 rpm for 30 s, followed by annealing at 120 °C for 10 min and 150 °C for 20 min. Then, the coated substrates were transferred to a N<sub>2</sub>-filled glovebox to deposit the perovskite onto the ETL using the aforementioned method. Next, 100  $\mu$ L of Spiro-OMeTAD in CB (72.3 mg·mL<sup>-1</sup>) containing additives of 17.5  $\mu$ L of bis(trifluoromethane)-sulfonimide lithium salt (520 mg·mL<sup>-1</sup> in acetonitrile) and 28.8  $\mu$ L of 4-*tert*-butylpyridine was spin-coated at 4000 rpm for 30 s as a hole transport layer. Finally, 80 nm of Au was deposited as a top electrode using a thermal evaporator system under a vacuum of  $\sim 10^{-4}$  Pa.

### 2.5 Characterization of perovskite films and devices

The absorption spectra were obtained by using a UV-Vis spectrophotometer (Perkin-Elmer, Lambda 365). X-ray diffraction (XRD) spectra were measured by a Rigaku MiniFlex 600 diffractometer equipped with a CuK $\alpha$  radiation at room temperature. The ultraviolet photoelectron spectra (UPS) for perovskite films were carried out by using X-ray Photoelectron Spectroscopy (Thermo Fisher, ESCALAB 250Xi). The root-mean-square (RMS) roughness of perovskite films was investigated by Scanning Probe Microscope (Bruker, Dimension Icon). The scanning electron microscopy (SEM) images were obtained by using the Field Emission Scanning Electron Microscope (SU-8010). The *J-V* curves were measured by using an Oriel Sol3A simulator (Newport) under AM 1.5 irradiation (100 mW·cm<sup>-2</sup>) and recorded by a Keithley 2400 source measurement unit. The light intensity was calibrated by a standard Si reference solar cell that has been certified by the National Renewable Energy Laboratory (NREL). The external quantum efficiency (EQE) measurements were conducted by using a Newport EQE measuring system. The active areas of the devices were fixed at 6.25 mm<sup>2</sup>. The unencapsulated 10 devices were tested and stored in the ambient under 65% RH.

## 3 RESULTS AND DISCUSSION

The DJ phase 2D perovskite (PDA)(MA)<sub>*n*-1</sub>Pb<sub>*n*</sub>I<sub>3*n*+1</sub> (nominal *n* = 4) was prepared from a stoichiometric (4:3:1) reaction between PbI<sub>2</sub>, MAI, and (PDA)I<sub>2</sub> (see Experimental section for details). In order to identify the difference between 2D and 3D perovskite films, the MAPbI<sub>3</sub> films were

also prepared for comparison. Fig. 2a shows the normalized absorption spectra for the 2D and 3D perovskite films. The optical bandgap ( $E_g$ ) can be deduced from the absorption edge according to  $E_g = 1240/\lambda$ , where  $\lambda$  is the absorption edge. The optical bandgaps of 2D and 3D perovskite films are 1.67 and 1.60 eV, respectively. X-ray diffraction (XRD) measurements were performed to study the crystallinity of 2D and 3D perovskite films. As shown in Fig. 2b, both of the perovskite films have two dominant peaks that appear around  $14.2^\circ$  and  $28.4^\circ$ , representing the diffraction from crystallographic planes (111) and (202), respectively<sup>[22, 30]</sup>. However, the peaks of the 3D perovskite film slightly shift towards large angles, which indicates the extension in crystal lattice constant. In the region between  $5^\circ$  and  $10^\circ$ , the 2D perovskite film shows the (040) and (060) peaks which characterize the 2D perovskites<sup>[30]</sup>. Ultraviolet photoelectron spectroscopy (UPS) was also conducted to identify the

difference between the 2D and 3D perovskite films on energy levels. The full UPS spectra are given in Fig. 2c. The magnified UPS spectra of the valence band edge ( $E_{\text{onset}}$ ) and the secondary electron cutoff edge ( $E_{\text{cutoff}}$ ) are depicted in Fig. 2d. As shown in Fig. 2d,  $E_{\text{cutoff}}$  values for the 2D and 3D perovskite films are 16.10 and 16.22 eV, respectively. Similarly, the 2D and 3D perovskite films have the same  $E_{\text{onset}}$  value of 1.77 eV. The highest occupied molecular orbital (HOMO) energy level can be calculated according to  $\text{HOMO} = 21.22 \text{ eV} - E_{\text{cutoff}} + E_{\text{onset}}$ , and the lowest unoccupied molecular orbital (LUMO) energy level can be calculated by the HOMO and optical bandgap<sup>[31]</sup>. Thus, the HOMO energy levels of 2D and 3D perovskite films are calculated to be  $-6.89$  and  $-6.77$  eV, respectively, with their corresponding LUMO energy levels to be  $-5.22$  and  $-5.17$  eV, respectively.

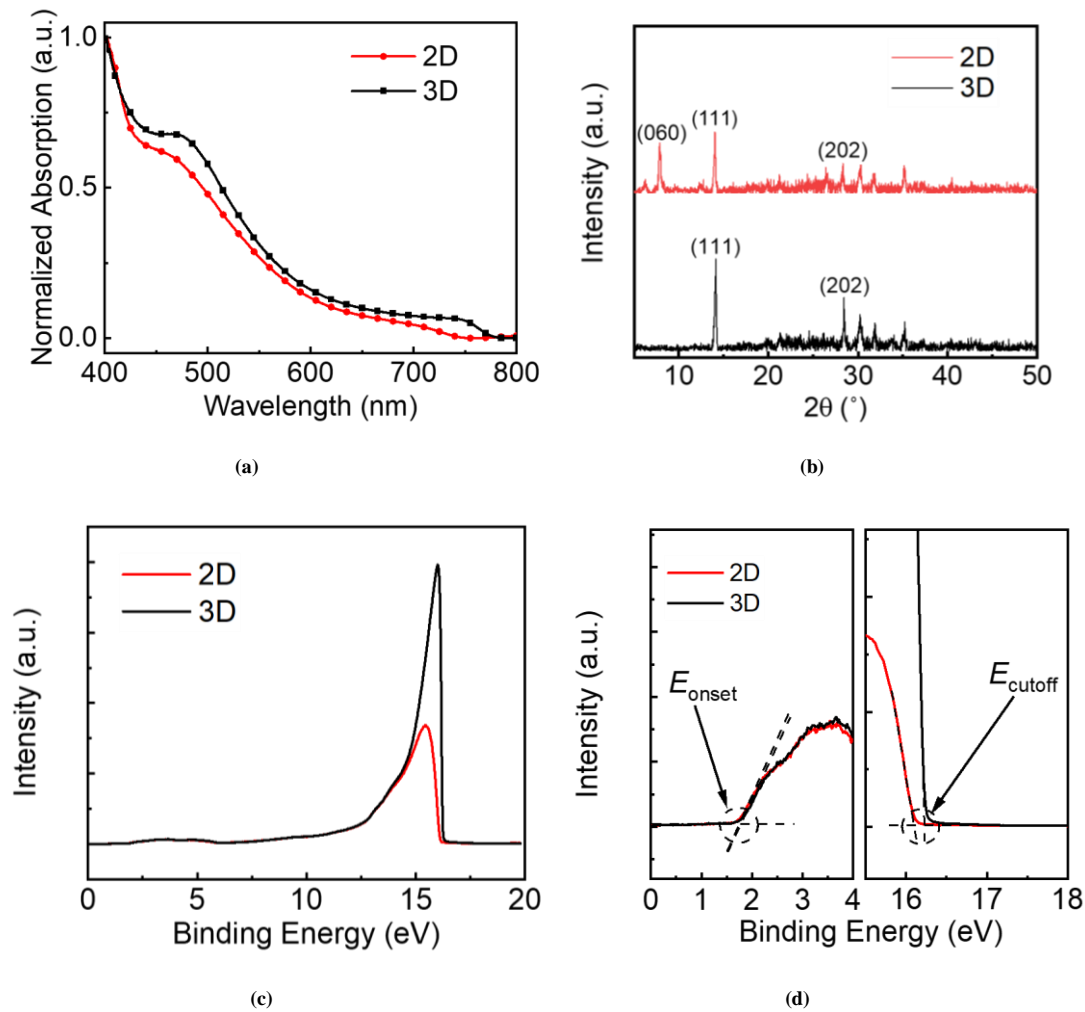


Fig. 2. (a) Absorption spectra of the 2D and 3D perovskite films. (b) X-ray diffraction (XRD) spectra of the 2D and 3D perovskite films. (c) Full UPS spectra of the 2D and 3D perovskite films. (d) UPS spectra for the valence band edge and secondary electron cutoff edge of the 2D and 3D perovskite films

We also studied the morphological evolution of 2D and 3D perovskite films by using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The SEM and AFM images of the 2D and 3D films are shown in Fig. 3. As shown in Fig. 3a, the grain size of 2D perovskite is about 50~200 nm, while the 3D perovskite has a larger grain size

up to 300 nm (Fig. 3b). The root-mean-square (RMS) roughnesses of the 2D and 3D films (Fig. 3c and d) are determined to be 4.13 and 7.41 nm, respectively, suggesting the smoother morphology of the 2D perovskite film. Besides, the 3D perovskite exhibited large grain, which is consistent with the SEM results.

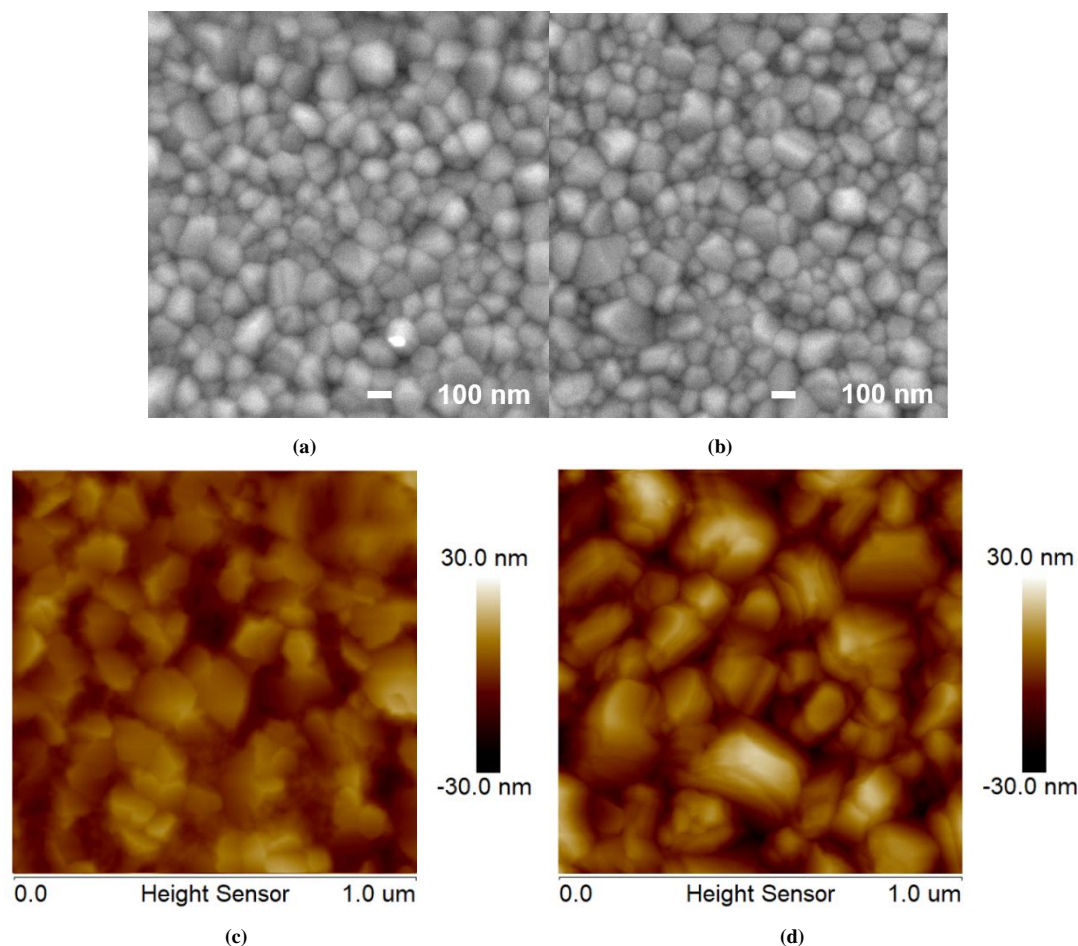


Fig. 3. SEM images of (a) 2D and (b) 3D perovskite films. The AFM images of (c) 2D and (d) 3D perovskite films

To investigate the photodetection performance of the (PDA)(MA)<sub>n-1</sub>PbI<sub>3n+1</sub> (*n* = 4) 2D perovskite material, photodiodes with a device architecture of ITO/SnO<sub>2</sub>/Perovskite/Spiro-OMeTAD/Au (as shown in Fig. 4a and Fig. S1) were fabricated. For comparison purposes, the photodiodes based on 3D perovskite were also fabricated with the same device configuration. To prepare the perovskite photodiode, SnO<sub>2</sub> was spin-coated on top of the ITO substrate as an ETL, and then the perovskite film was deposited on the ETL. Later, Spiro-OMeTAD was spin-coated onto the perovskite layer as a hole transport layer (HTL) followed by the sequentially thermal evaporation of Au as a top electrode. To explore the difference between the devices based on 2D and 3D perovskite films, we tested the external quantum efficiencies

(EQEs) of the perovskite photodiodes. The corresponding EQE spectra of the devices are shown in Fig. 4b. The photoresponse range of the devices based on the 2D perovskite is 300~750 nm, which is narrower than that of the 3D devices (300~800 nm). The trend of EQE spectra is consistent with that of the absorption spectra. The maximum EQE for the devices based on the 3D perovskite film is 77% at 470 nm, which is higher than that of the 2D devices (67% at 460 nm). The lower EQE for the devices based on 2D perovskite film can be attributed to the existence of the insulating PDA layers which hinder the charge transport. As shown in Fig. 4c, the dark current densities of the photodiodes based on 2D and 3D perovskite films are  $9.60 \times 10^{-4}$  and  $3.84 \times 10^{-3}$  mA·cm<sup>-2</sup>, respectively. The dark

current of devices based on the 2D perovskite film is much lower than that of the 3D ones, which is beneficial to improve the on/off ratio of photodiodes. The photocurrent of devices based on the 3D perovskite is higher than that of the 2D devices (Fig. 4d), which is consistent with the results

reported in the literature<sup>[28]</sup>. The on/off ratio determined by  $I_{\text{photo}}/I_{\text{dark}}$  is  $3.10 \times 10^5$  for the device based on the 2D perovskite film. Owing to its low dark current, the on/off ratio for the 2D perovskite-based device is much higher than that of the 3D device ( $7.40 \times 10^3$ ).

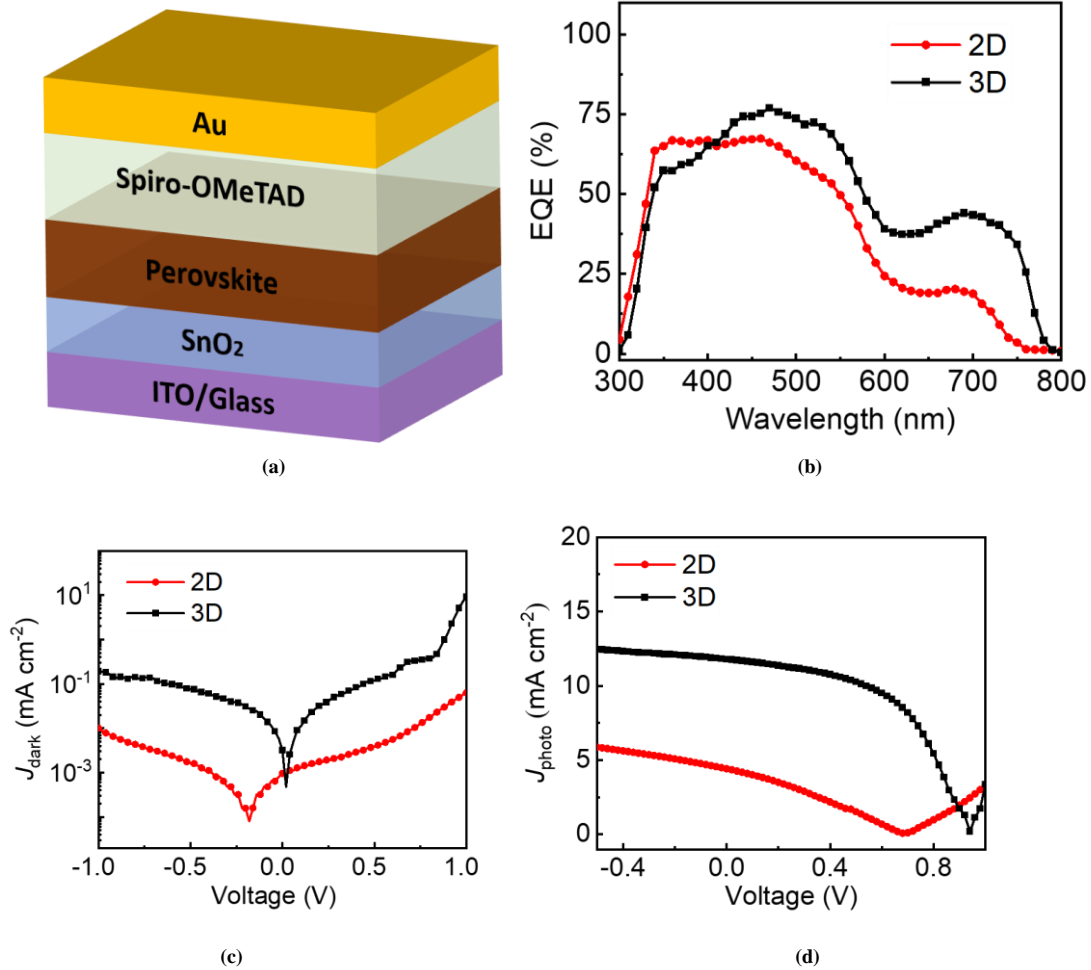


Fig. 4. (a) Configuration of the photodiode. (b) EQE spectra, (c) dark current density, and (d) photocurrent density of the photodiodes based on 2D and 3D perovskite films measured under one solar (AM 1.5G, 100 mW·cm<sup>-2</sup>) illumination

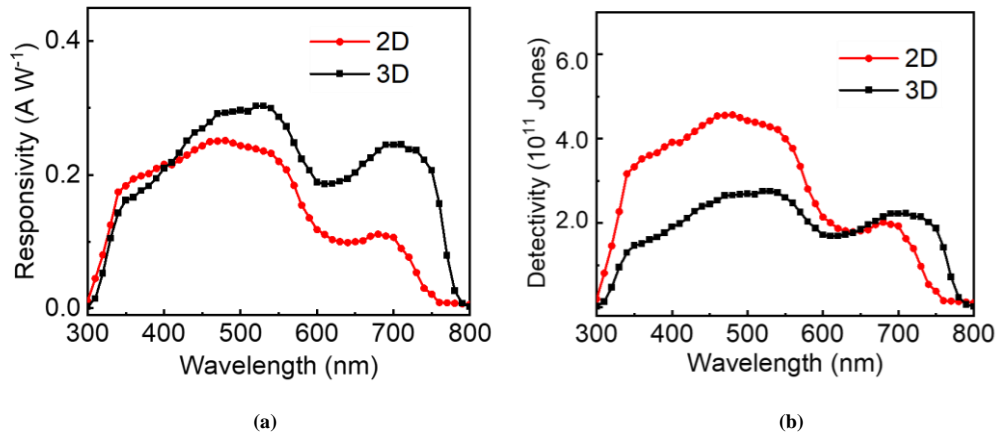


Fig. 5. (a) Responsivity, and (b) detectivity of photodiodes based on the 2D and 3D perovskite films measured under one solar (AM 1.5G, 100 mW·cm<sup>-2</sup>) illumination

According to the definition, the responsibility is the ratio of photocurrent to the incident-light intensity, indicating the ability of a device in response to the optical signal. Thereafter, it can be given as follows<sup>[16, 32]</sup>:

$$R = \frac{J_{\text{photo}}}{L_{\text{light}}} \quad (1)$$

where  $R$  is the spectral responsivity,  $J_{\text{photo}}$  the photocurrent density and  $L_{\text{light}}$  the incident light intensity. Since EQE can be calculated by the number of photo-generated electrons divided by the number of incident photons, equation (1) can also be described by the following equation (2):

$$R(\lambda) = \frac{EQE \cdot q\lambda}{hc} \quad (2)$$

where  $q$  is the electron charge,  $\lambda$  the corresponding wavelength of light,  $h$  the Planck's constant, and  $c$  the light speed. Using the measured EQE results, we can calculate the wavelength-dependent responsibility of the perovskite photodiodes through equation (2). The highest responsivity data of the perovskite photodiodes were  $0.25 \text{ A}\cdot\text{W}^{-1}$  at 480 nm and  $0.30 \text{ A}\cdot\text{W}^{-1}$  at 530 nm for 2D and 3D perovskites, respectively (Fig. 5a). The high charge accumulation and increased recombination losses will hinder the photoelectric performance. Thus, the responsivity of the device based on 2D perovskite is lower than that of the 3D perovskite-based counterpart. Another parameter to evaluate the characteristics of the photodiode is detectivity ( $D$ ). The detectivity characterizes how weak the light can be detected. It is determined by the responsivity and the dark current of a photodetector. In general, the detectivity can be calculated

by equation (3):

$$D(\lambda) = \frac{R(\lambda)}{\sqrt{2qJ_d}} \quad (3)$$

where  $q$  is the electron charge and  $J_d$  the dark current density. Considering all of the above equations, a high EQE along with a low dark current can promote the detectivity of a photodetector. The device based on 2D perovskite films showed the highest detectivity of  $4.57 \times 10^{11}$  Jones at 480 nm, which is higher than that of 3D perovskite-based counterpart ( $2.76 \times 10^{11}$  Jones at 530 nm). Although the higher EQE and responsivity were obtained in the devices based on 3D perovskite film, the devices based on 2D perovskite film exhibited higher detectivity than the 3D perovskite-based devices. It can be due to the fact that the organic cation ( $\text{PDA}^+$ ) in the perovskite crystalline structure reduces the dark current. However, the organic cation can also result in the reduction of photocurrent. Therefore, an appropriate amount of organic cations should be used in order to achieve the balance between the photo and dark current. The performance parameters of the devices based on 2D and 3D perovskite films are summarized in Table 1. Furthermore, we summarized the performance parameters of our and others' work in Table 2. It is shown that the on/off ratio was ultrahigh for the devices based on 2D perovskite film in this work, which is 2~3 orders of magnitude higher than the values of the other reported photodetectors based on the DJ phase 2D perovskites<sup>[28, 29]</sup>. Meanwhile, the responsivity and detectivity of 2D perovskite-based devices are higher than the reports of DJ-type perovskites.

**Table 1. Photodetection Performance Parameters for the Devices Based on 2D and 3D Perovskite Films**

Perovskite	Dark current density ( $\text{mA}\cdot\text{cm}^{-2}$ @ 0V bias)	Responsivity ( $\text{A}\cdot\text{W}^{-1}$ @ 0V bias)	Detectivity (Jones @ 0V bias)	On/off ratio (@ 0V bias)	Maximum on/off ratio
2D	$9.60 \times 10^{-4}$	0.25	$4.57 \times 10^{11}$	$4.60 \times 10^3$	$3.10 \times 10^5$ (@ -0.1 V bias)
3D	$3.84 \times 10^{-3}$	0.30	$2.76 \times 10^{11}$	$3.07 \times 10^3$	$7.40 \times 10^3$ (@ -0.02 V bias)

**Table 2. Comparison of Performance Parameters for the Photodetectors Based on 2D DJ Perovskites**

Perovskite	Dark current (A)	Responsivity ( $\text{mA}\cdot\text{W}^{-1}$ )	Detectivity (Jones)	On/off ratio	Response time	Ref.
(AMP)(MA)Pb <sub>2</sub> I <sub>7</sub>	N/A	0.16 at 532 nm	$5.00 \times 10^{10}$	$6.32 \times 10^2$	40 ms	[28]
EDA(MA) <sub>3</sub> Pb <sub>4</sub> I <sub>13</sub>	$3.3 \times 10^{-10}$	125	$7.10 \times 10^{10}$	$7.50 \times 10^2$	410/380 $\mu\text{s}$	[29]
PDA(MA) <sub>3</sub> Pb <sub>4</sub> I <sub>13</sub>	$6.0 \times 10^{-8}$	250 at 480 nm	$4.56 \times 10^{11}$	$3.10 \times 10^5$	20/45 ms	This work



As can be seen from Table 1, the photodiodes based on 2D perovskite displayed better performance with a lower dark current, higher detectivity and on/off ratio. Since stability is the most prominent advantage of 2D perovskite materials compared to 3D ones, the stability of both unencapsulated devices was investigated under ambient condition (65% RH). The normalized photocurrent densities and the dark current densities of two types of photodiodes as a function of time are shown in Fig. 6. As shown in Fig. 6a, the normalized photocurrent density of the 3D perovskite-photodiode showed a great decrease and only maintained 35% of the initial photocurrent value after 90 days of storage. In contrast,

the 2D perovskite-photodiode exhibited significantly improved stability with 95% of the initial photocurrent under the same storage condition. Fig. 6b shows the dark current densities of the two types of devices as a function of time. The dark current density of the devices based on 2D perovskites maintained  $\sim 10^{-4}$  mA·cm $^{-2}$  all along, while that of the 3D ones increased from  $3.84 \times 10^{-3}$  mA·cm $^{-2}$  to  $5.80 \times 10^{-3}$  mA·cm $^{-2}$  after 90 days. It is well known that the increase of dark current is detrimental to the device performance. Therefore, the devices based on 2D perovskites are more promising in practical applications.

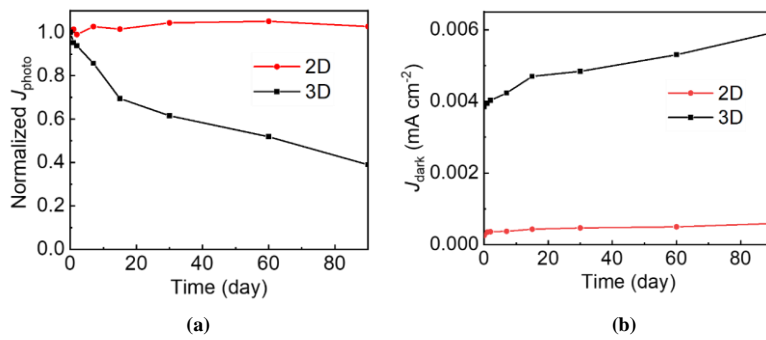


Fig. 6. (a) Normalized photocurrent density, (b) the dark current density of the photodiodes based on 2D and 3D perovskite films as a function of the storage time

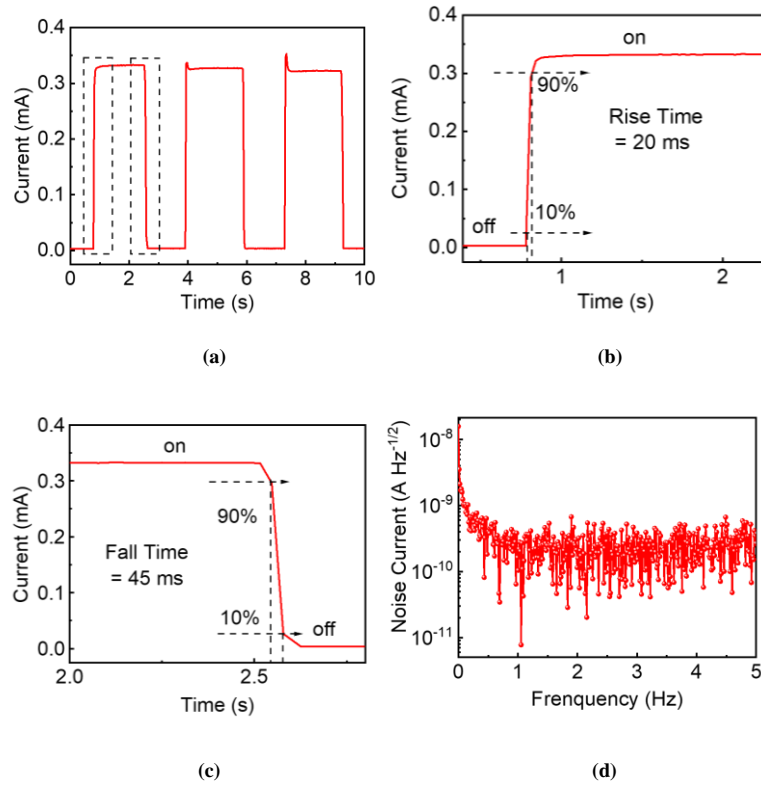


Fig. 7. Photoresponse performance of photodiodes based on 2D perovskite film measured under the repeated cycles of illumination of one solar light (100 mW·cm $^{-2}$ , AM 1.5G). (a) Time-dependent photocurrent response ( $I-t$ ) curves. (b) Rise time. (c) Fall time. (d) The noise current measured under one solar (100 mW·cm $^{-2}$ , AM 1.5 G) illumination



We further investigated the light response speed of the photodiode based on 2D perovskite film by testing the response time of the device under one solar light illumination (Figs. 7a and S2). Fig. 7a shows the time-dependent photocurrent response curves within 10 s under switching state. Fig. 7b and c show the rise and fall time of the photodiode, respectively. The rise time (fall time) is defined as the time for the photocurrent to rise from 10% to 90% (fall from 90% to 10%) of the maximum value during the on and off cycles<sup>[31, 33, 34]</sup>. The calculated rise time for the

2D perovskite-based photodiode is 20 ms and the fall time is 45 ms, which exhibited comparable response time with the devices reported by others<sup>[25, 28]</sup>. The fast rise and fall time suggested the fast response speed of the devices based on 2D perovskite. Fig. 7d shows the level of the noise current of the 2D perovskite-based photodiode. It is found that the overall noise current is stable at  $10^{-9} \sim 10^{-10} \text{ A}\cdot\text{Hz}^{-1/2}$ . Moreover, the noise current stabilized quickly at low frequencies (within 5 Hz), which is also of great significance for the practical application of the photodiodes. The highest on/off ratio of the device based on 2D perovskite is  $3.10 \times 10^5$ , which is impressive for 2D perovskite-based photodiodes. The unencapsulated photodiodes based on 2D perovskite can be stored under air with RH of 65% for over 90 days without significant degradation, showing their improved stability than the 3D perovskite-based photodiodes. This long-term stable 2D Dion-Jacobson phase perovskite photodiode with low dark current and high on/off ratio is promising for the practical switching applications.

#### 4 CONCLUSION

In summary, we incorporated a diamine (PDA) into the conventional 3D perovskite component to form a DJ phase 2D perovskite PDA(MA)<sub>n-1</sub>Pb<sub>n</sub>I<sub>3n+1</sub> (nominal  $n = 4$ ). The photodiode based on 2D perovskite exhibited better performance with a high detectivity ( $4.57 \times 10^{11}$  Jones at 480 nm) and a low dark current density ( $9.60 \times 10^{-4} \text{ mA}\cdot\text{cm}^{-2}$ ) in comparison with the device based on 3D perovskite. Also,

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