Self-powered perovskite/CdS heterostructure photodetectors

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ABSTRACT

1 Methylammonium lead halide perovskites have attracted enormous attention due to their
2 remarkable physical properties and potential for numerous (opto)electronic applications. Here,
3 high-performance photodetectors based on $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI_3)/CdS heterostructures, are
4 demonstrated. The resulting self-powered MAPbI_3 /CdS photodetectors show excellent
5 operating characteristics including a maximum detectivity of 2.3×10^{11} Jones, responsivity of
6 0.43 A/W (both measured at 730 nm) and temporal response time of <14 ms. The mechanisms
7 of charge separation and transport at the interface of the MAPbI_3 /CdS junction were
8 investigated via conductive and photoconductive atomic force microscopy (C-AFM and PC-
9 AFM). Obtained results show that grain boundaries exhibit higher photocurrent than flat regions
10 of the top perovskite layer, which indicates that excitons preferentially separate at the edges of
11 the perovskite crystals i.e. at the grain boundaries. The study of the photoelectric mechanism at
12 the nanoscale provides essential insights for the fabrication of high-performance perovskite-
13 based photodetectors, where the device performance could potentially be fine tuned through
14 grain boundary engineering. The demonstrated self-powered photodetector are promising for
15 numerous applications in low-energy consumption optoelectronic devices.

25 INTRODUCTION

1 Methylammonium lead trihalide perovskite materials (MAPbX_3 , $\text{MA}=\text{CH}_3\text{NH}_3^+$; $\text{X}=\text{halogen}$)
2 have drawn increasing attention due to their long diffusion lengths, high light absorption
3 coefficients and low intergap trap density.¹⁻³ In the past several years, hybrid perovskites were
4 shown great promise for photovoltaic applications where the power conversion efficiency
5 (PCE) of MAPbX_3 based solar cells (PSCs) has increased from 3.8% to over 22.1%.⁴⁻⁷ In
6 addition, high-quality perovskite films can be synthesized via several rapid and simple methods,
7 such as spin coating,⁸ spray coating,^{9,10} slit-casting¹¹ and blade coating,¹²⁻¹⁵ which can be
8 adapted to large-scale fabrication. These merits including simple fabrication processing and
9 outstanding optoelectronic properties make perovskites the most promising amongst emerging
10 photovoltaic technologies. More recently, the use of MAPbX_3 perovskites has been extended
11 to photodetectors, i.e. devices that convert incident optical signals to electrical signals that are
12 key components for numerous modern applications, hence paving the way to new research
13 directions.^{16,17}

14 Numerous recent studies have revealed that the performance of photovoltaic cells is highly
15 dependent on the interfacial properties between the electron transport layer (ETL) and the
16 perovskite.¹⁸⁻²⁰ An ideal ETL should provide conformal contact with the perovskite film and
17 reduce the concentration of surface defects/traps.²¹⁻²⁷ Moreover, the existence of a built-in
18 potential at the heterointerface is desirable as it can effectively suppress the carrier
19 recombination.²⁸ Therefore, identifying suitable ETL systems is important for improving the
20 performance of both solar cells and photodetectors. To this end, CdS is a well studied n-type
21 semiconductor for solar cells and photodetectors with suitable energy band structure aligned
22 with $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI_3).²⁹ Compared to other widely used ETL materials such as TiO_2 ,
23 CdS shows significant higher electron mobility,³⁰ and unlike TiO_2 it doesn't suffer from oxygen
24 vacancies-induced charge traps caused upon illumination with ultraviolet light.³¹⁻³³ Previously,
25 Juarez-Perez *et al.* have grown CdS thin film via sputtering, and incorporated them as ETL in
26 PSCs. However, the CdS electron layer introduces a huge resistance, and consequently results

in a low fill factor and the PCE is only 1.53%.³⁰ Similarly, Hwang *et al.* have used thermally evaporated CdS as ETLs in PSCs with significantly higher PCE of 12.2%.³⁴ In their work CdS PSC performed enhanced photostability (maintained 91% of its initial efficiency) under continuous sunlight illumination for 12 h, while the traditional TiO₂ based PSC lost 82% of its initial efficiency. Finally, in order to improve the crystallinity Peng *et al.* employed chemical bath deposited (CBD) CdS as ETLs in PSC. The CdS PSC showed improved open-circuit voltage with PCE of 16.1%.³⁵

Here, heterostructured photodetector based on CdS and MAPbI₃ perovskite were fabricated and studied. The resulting devices showed excellent performance, with maximum on/off current ratio of $\sim 1.13 \times 10^5$ (at 0 V), specific detectivity of $\sim 9.79 \times 10^{10}$ Jones (at 0 V) and PCE of $\sim 10.05\%$. The role of CdS on the charge photogeneration and transport across in the MAPbI₃/CdS heterojunction was thoroughly studied using conductive and photoconductive atomic force microscopy (C-AFM and PC-AFM).³⁶⁻⁴⁰ The work highlights MAPbI₃/CdS as a promising heterojunction for various emerging applications.

Figure 1. (a) Schematic illustration of the fabrication process of MAPbI₃/CdS heterojunction. (b) Raman spectra of the CdS on ITO. (c) XRD spectra of the MAPbI₃/CdS heterojunction. (d) PL spectra of pure MAPbI₃ film and MAPbI₃/CdS heterojunction.

RESULTS AND DISCUSSION

Preparation of MAPbI₃/CdS Bilayer. Figure 1a shows the fabrication process of the MAPbI₃/CdS heterojunction. The CdS was grown via CBD method (Figure 1a). The thickness of the CdS film can be tuned by changing the deposition time. Figure 1b displays the Raman spectra of a representative CdS layer. The Raman peak at 301 cm⁻¹ originates from the A₁ (LO) mode (where LO stands for longitudinal optical phonon) and its overtone at 602 cm⁻¹ proving the successful synthesis of CdS.⁴¹

MAPbI₃ was then deposited atop CdS via one-step spin-coating method (Figure 1a). X-ray diffraction (XRD) measurements were also performed and provided further evidence of the presence of the CdS and MAPbI₃ when deposited on ITO (Figure 1c). The diffraction peaks of CdS indium tin oxide (ITO) (transparent electrode),²⁸ and MAPbI₃.^{42,43} are indicated by the yellow, green and blue bars,⁴¹ respectively. None of the PbI₂ peaks were observed in the XRD data, indicating the good quality of MAPbI₃ layer.

Figure 1d exhibits the PL spectra for the MAPbI₃ and MAPbI₃/CdS heterojunction excited using a 532 nm laser. Both samples show strong PL signal with peak at 778 nm which is consistent with the PL feature of pristine MAPbI₃.^{44,45} However, the intensity of the PL signal of the MAPbI₃/CdS heterojunction was significantly lower than that for the pristine MAPbI₃. This dramatic PL reduction is attributed to the efficient charge transfer occurring between the metal halide perovskite and CdS,^{24,26} and will be discussed next.

Figure 2. The time resolved PL decay curves. (a) MAPbI₃ film. (b) MAPbI₃/CdS bilayer. (c) The time resolved PL decay curves of MAPbI₃/CdS bilayer with biexponential fits showing a fast (≈ 14.9 ns) and a slow transient (≈ 42.7 ns).

In an effort to better understand the charge carrier dynamics at the MAPbI₃/CdS heterointerface, time-resolved PL measurements were performed (Figure 2). The time-resolved traces represent the transient evolution of the electron-hole population after impulsive photoexcitation, and the measured transient decay process of the excited state can be fitted using:

$$I_{(t)} = I_0 \sum_i w_i \exp\left(-\frac{t}{\tau_i}\right) \quad (1)$$

where I_0 is the initial intensity, w_i is i^{th} amplitude, τ_i is the lifetime.⁴⁶ As shown in Figure 2a, $i=1$ was utilized for the pristine MAPbI₃ due to its single exponential decay. The fitting yields a lifetime of 43.5 ns, which is close to previously reported values.^{47,48} For the MAPbI₃/CdS heterojunction as shown in Figure 2b, the charge carrier lifetime decreased obviously and biexponential decay, where $i=2$, was used for the fitting. Analysis of the fitting in Figure 2b yields times for the fast part of the decay of 14.9 ns and 42.7 ns for the slower part as shown in Figure 2c. These times are attributed to the different lifetimes of photocarriers on the surface and in the bulk, respectively.^{49,50} To this end, the faster PL decay indicates efficient charge transfer at the heterointerface⁵¹ in agreement with the significantly quenched PL signal seen in Figure 1d. On the basis of this data we conclude that the formed MAPbI₃/CdS heterointerface promotes efficient charge transfer.⁵²

Figure 3. (a) Photograph of the photodetector made by MAPbI₃/CdS heterojunction. (b) Schematic diagram of the device. (c) Energy band diagram of the MAPbI₃/CdS heterojunction photodetector.

Fabrication of MAPbI₃/CdS Heterojunction Photodetector.

Photodetector devices consisting of ITO/CdS/MAPbI₃/Au (Figure 3a-b), were fabricated with the CdS layer functioning as the ETL. Reference devices based on MAPbI₃-only and CdS-only were also prepared in parallel (see Figure S1). Optimal device performance was achieved by carefully tuning the thickness of CdS and MAPbI₃ layers as shown in Figures S2 and S3 (relevant discussion in Note S1). The optimum thicknesses of CdS and MAPbI₃ were determined to be ~55 nm and ~378 nm, respectively. From the energy band diagram in Figure 3c, the conduction band of CdS is ~0.3 eV lower than that of MAPbI₃. This large energy offset suggests that the CdS ETL can indeed accept electrons that eventually be transported to the ITO electrode, while simultaneously blocking holes at the MAPbI₃/CdS interface.⁵³ These results are in excellent agreement with the PL data shown in Figure 1d and Figure 2b.

Measurements of the Device Performance.

The built-in field presents at the MAPbI₃/CdS interface (Figure 3b) is expected to enhance the photoresponse of the detector. In Figure 4a, we present the I-V curves of the MAPbI₃/CdS photodetectors measured in the dark and under various white light illumination intensities with the corresponding linear I-V curves shown in Figure S4a. The device based on the MAPbI₃/CdS heterointerface show clear photovoltaic action with an open circuit voltage ~0.75 V. Moreover, the photocurrent is significantly increased as compared to the MAPbI₃-only device shown in Figure 4b (the linear dark I-V curves are shown in Figure S4b). It should be noted that the CdS-only device shows much weaker photocurrent compared with MAPbI₃-only device (Figure S5). Therefore, the enhanced photocurrent measured for the MAPbI₃/CdS device can be attributed to the efficient charge separation at the MAPbI₃/CdS heterointerface, in excellent agreement with the afore mentioned PL results.

Responsivity (R) and detectivity (D) are the two important parameters used to evaluate the performance of the photodetector. The responsivity of the detector can be obtained using:

Figure 4. (a) I-V curves of the heterojunction photodetector in dark and under different illumination intensities. (b) Corresponding I-V curves of MAPbI₃-only device. (c) Photocurrent and photoresponsivity of the heterojunction photodetector measured under 0 V. (d) Detectivity of the MAPbI₃/CdS photodetector under 0 V. (e) On/off ratios measured on different voltages of MAPbI₃/CdS photodetector and MAPbI₃-only device. (f) J-V characteristics of the MAPbI₃/CdS photodetector under simulated AM 1.5 G solar irradiation.

$$R = \frac{I_{\text{Photo}} - I_{\text{Dark}}}{P_{\text{in}} * A} \quad (2)$$

where P_{in} is incident light intensity, I_{dark} is the dark current and I_{photo} is the measured photocurrent.⁵⁴ The noise current and noise equivalent power were also measured in order to evaluate the photodetector performance (see Note S2 and Figure S6). Through the analysis of the noise current, the specific detectivity can be evaluated using:

$$D = \frac{R\sqrt{A}}{\sqrt{2qI_{\text{Dark}}}} \quad (3)$$

where q is elementary charge and A is the active area (0.02 cm²) of the device.⁵⁵

Figure 4c-d show the photocurrent, photoresponsivity and detectivity of the MAPbI₃/CdS photodetector evaluated at 0 V. For comparison, the same parameters measured at 1.5 V are also presented in Figure S7. Under illumination intensity of 0.68 mW/cm², the MAPbI₃/CdS photodetector exhibits a responsivity of 0.183 A/W under 0 V and 4.45 A/W at 1.5 V. The detectivity measured under illumination intensity of 0.68 mW/cm² for the MAPbI₃/CdS photodetector is 9.79×10¹⁰ Jones at 0 V, and reduces to 6.36×10¹⁰ Jones at 1.5 V due to increased I_{dark} . Figure 4e exhibits the bias dependence of current on/off ratio. At a bias voltage of ~0 V, the on/off ratio reaches the highest value of 1.13×10⁵ under 0.68 mW/cm² light illumination. When the MAPbI₃/CdS heterojunction device was operated as a solar cell (fourth quadrant of the I-V curves), a power conversion efficiency of 10.05% was calculated under 100 mW/cm² AM 1.5 simulated solar radiation (Figure 4f), which demonstrates the self-powered

performance of the MAPbI₃/CdS heterojunction device. A higher PCE could be reached by carefully selecting suitable hole transport layers that assist the hole-electron pair separation and charge extraction.

The I-V curves measured under different illumination wavelengths in the range of 405-850 nm and at a constant illumination power of 10 mW/cm² for a representative MAPbI₃/CdS photodetector, are shown in Figure 5a. Figure 5b shows the ultraviolet-visible (UV-Vis) absorption spectra of the CdS film, perovskite film and MAPbI₃/CdS hybrid system. When the MAPbI₃/CdS photodetector is excited with light of 405, 488, 550, 610 and 715 nm, the photocurrent of the MAPbI₃/CdS photodetector is clearly enhanced as compared to the dark current. Interestingly, no obvious increase in the photocurrent upon excitation at 850 nm is observed in line with the absorption spectrum of the MAPbI₃/CdS hybrid system (Figure 5b). Since CdS has a bandgap ~2.4 eV (Figure 3c), absorption should only occur at wavelengths shorter than ~520 nm. Indeed, the introduction of CdS enhances the absorption region of MAPbI₃ film especially from 350 nm to 523 nm as shown in Figure 5b. As shown in Figure 5c, the MAPbI₃/CdS device yields a relatively high external quantum efficiency (EQE) of over 65% in the 360-630 nm range. Meanwhile, the drop-off in the EQE curve above 800 nm indicates that the photons with wavelength longer than 800 nm are not efficiently absorbed. Figure 5c and Figure S8 show the responsivity (green line) and detectivity for the device. The responsivity can be calculated by the relationship: $EQE = R \times E \times 100$, where E is the incident photon energy. On the other hand, D can be obtained by using Eq. 3. For illumination wavelengths over 800 nm, both the R and D exhibit a significant drop. The maximum values of D and R are 2.3×10^{11} Jones and 0.43 A/W, respectively, measured at 730 nm under 10 mW/cm² illumination intensity.

Figure 5. (a) I-V curves under different illumination wavelengths. **(b)** UV-VIS absorption spectra of the pure CdS film, pure MAPbI₃ film and MAPbI₃/CdS hybrid films. **(c)** EQE and responsivity of MAPbI₃/CdS photodetector.

Finally, the temporal response of the heterojunction MAPbI₃/CdS photodetector to white light pulses (40 mW/cm²) was investigated. Figure 6 exhibits the time dependence photoresponse of the device biased at 1.5 V. Figure 6a shows that the light-induced on/off switching is consistent and repeatable over multiple cycles. Figure 6b shows one cycle of the temporal photoresponse, from which the rise and decay times were calculated yielding 3.2 and 9.6 ms, respectively. Evidently, the temporal photoresponse of the MAPbI₃/CdS photodetector is faster than that of MAPbI₃-only and CdS-only device. We ascribe this to the efficient charge transfer at the heterointerface. In terms of response speed, we note that our MAPbI₃/CdS photodetector is approximately three orders of magnitude faster than the perovskite/graphene photodetector reported previously,⁵⁶ and one order of magnitude faster than state-of-art nanostructured perovskite photodetector.⁵⁷ The only faster metal halide perovskite photodetector reported to date is the recently demonstrated nano-gap photodetectors by Georgiadou *et al.*,⁵⁸ where the transit time of the photogenerated charge carriers was substantially reduced owing to the nanoscale interelectrode distance. Despite that, our proposed MAPbI₃/CdS photodetector concept offer numerous advantages including high responsivity, specific detectivity and high self-powered performance with the potential for further improvements.

Figure 6. (a) Photoswitching characteristics of the three types of photodetectors under chopped light irradiation. **(b)** Temporal photocurrent response for the three types of photodetectors.

Carrier Transport Study in MAPbI₃/CdS Heterojunction in the Dark. In view of the promising potential of the MAPbI₃/CdS heterojunction, we further explored the photoelectric mechanism of MAPbI₃/CdS heterojunction using C-AFM and PC-AFM techniques. Photocurrent mapping using these techniques can provide valuable information regarding the relationship between the heterojunction morphology and charge transport in the nanoscale.³⁶⁻⁴⁰ Figure 7a shows the schematic diagram of the C-AFM and PC-AFM setups. A Pt-Ir-coated tip was used for C-AFM and PC-AFM measurements. The ITO was then biased with a voltage while the conductive AFM tip was grounded.

Figure 7. (a) Schematic illustration of the PC-AFM instrument. (b) Energy band diagram of the tip, MAPbI₃, CdS and ITO. (c) AFM topographic image of MAPbI₃/CdS heterojunction. (d) Schematic illustration of the MAPbI₃/CdS surface with cavities as shown in image c. (e) Fitting I-V curves extracted at the regions 1-9 shown in d. (f) Image of photocurrent mapping. (g) Schematic illustration of the proposed photocarriers transport mechanism. (h) Voltage

dependent photoresponse curves corresponding to region 1 and selected areas from interiors and edges of region 2, 6 and 7.

A series of current maps were acquired under different applied voltages in the range of -1.8 V to +1.8 V (Figure S9). The brighter (darker) areas in the current mapping indicate the higher absolute current under positive (negative) bias. The corresponding AFM topographic image is shown in Figure 7c. We identify the presence of several cavities in the perovskite layer marked as the nine regions shown in Figure 7d. Those cavities are formed by perovskite crystals with exposed grain boundaries of perovskite crystals, allowing us to compare the spatial dependence of photocurrent generation in the perovskite thin film. The point I-V curves measured from these nine regions are plotted in Figure 7e, with the error bars representing the standard deviations. Due to the p-type nature of MAPbI₃ and the n-type nature of CdS (Figure 7b), the measured I-V curves exhibit p/n-like rectifying characteristic.

In an effort to understand the nature of the charge transport mechanism, the point I-V curves were fitted with the thermionic emission model. Previously, Li *et al.* have used thermionic emission to describe the carrier transport between MoS₂ and an AFM tip⁵⁹:

$$I = I_0 \left[\exp \left(\frac{qV}{\eta k_B T} \right) - 1 \right] \quad (4)$$

where I_0 is the saturation current, V is the applied sample bias, k_B is the Boltzmann constant, q is the electronic charge, η is the ideality factor, and T is the temperature. Alternatively, the equation can also be presented as:

$$I_0 = A_e A^* T^2 \exp \left(-\frac{q \Phi_B}{K_B T} \right) \quad (5)$$

where A^* is the Richardson constant (defined in the Note S3), A_e is the effective contact area obtained by Hertz contact theory (Note S4 and Figure S10).

As shown in Figure 7e, the current fittings suggest the carrier transport follows the thermionic emission theory very well. In addition, in thermionic emission theory, the barrier height Φ_B can be determined using:

$$\Phi_B = \frac{k_B T}{q} \ln\left(\frac{A^* A_e T^2}{I_0}\right) \quad (6)$$

Based on the equations above, Table 1 gives the calculated effective barrier height Φ_B of the nine regions marked in Figure 7d .

Table 1: Φ_B of the eight cavities and flat region.

Region	1	2	3	4	5	6	7	8	9
Φ_B/eV	0.85	0.80	0.78	0.76	0.79	0.82	0.79	0.77	0.74

The value of Φ_B for the eight cavities is consistently smaller than that of the flat region due to the short transport distance of the cavity area to the bottom of the MAPbI₃/CdS interface. In addition, the ideality factor η can be calculated using:

$$\frac{1}{\eta} = \frac{k_B T}{q} \frac{d(\ln I)}{dV} \quad (7)$$

where the value of η can be used to estimate the deviation of carrier transport process from the ideal thermal emission. Herein, η of the nine regions ranges from 5.35 to 5.86 (shown in Figure S11). The relatively high η is likely attributable to non-idealities such as defects at the perovskite surface.²⁸

Study of the Photoelectric Mechanism in MAPbI₃/CdS Heterojunctions. The sample regions highlighted in Figure 7d were also studied by PC-AFM in order to compare the charge transport with photocurrent characteristics. Figure S12 shows the photocurrent maps obtained at different applied sample potentials measured under 405 nm laser illumination. The results reveal obvious current enhancement compared with the corresponding dark current at the same voltage (see Figure S9). The photocurrent map under a bias voltage of 0.2 V is shown in Figure

7f. Interestingly, the photocurrent near the apparent cavities (indicated as regions 2-9 in Figure 7d) appears enhanced by several times compared with the flatter regions atop the perovskite layer (region 1). The photocurrent around the edges of the cavities also appears higher.

We further analyzed the photoresponse from the inner area and edges of the cavities present on the perovskite film. Figure S13 shows photoresponse mappings of the MAPbI₃/CdS heterostructure. Here, the photoresponse was defined as:

$$\text{Photoresponse} = \frac{(I_{\text{Photo}} - I_{\text{Dark}}) / q}{P_{\text{in}} / h\nu} \quad (8)$$

where I_{Dark} is dark current, I_{Photo} is photocurrent, q is elementary charge, P_{in} is the optical power and $h\nu$ is the photon energy. The photoresponse images were then generated by NanoScope-Analysis software package using Eq. 8.

The voltage dependent photoresponse curves were plotted by extracting the average photoresponse values from “region 1”, and selected areas from interiors and edges of “region 2, 6, and 7” as shown in Figure 7h. All curves exhibit an open circuit voltage of ~0.7 V, where a minimum photoresponse value is obtained. This photovoltaic phenomenon agrees well with the results obtained from the I-V feature of MAPbI₃/CdS photodetector mentioned above. These photoresponse curves rise linearly in the voltage range from -0.7 V to 1.8 V due to the increasing of the forward voltage. Moreover, “hot spots” observed in the photocurrent image (Figure 7f) are distributed along the edges of the cavities, which indicates a high photoresponse for these specific edge areas. On the other hand, the flat region (region 1) exhibits the lowest photoresponse. It should be noted that tip convolution effects may play a role in the photocurrent mapping. For example, the conductive AFM tip could be in better contact with the edges than with the surface of the layer, leading to a larger contact area and as higher currents. In order to eliminate tip convolution effects, all the photocurrent mappings were obtained through superior force control of the AFM tip (PeakForce TUNA, Bruker). A pN-level tip-sample interaction force was applied for the PC-AFM experiments, which is significantly

lower than typically used with tapping mode (~ 1 nN). The tip-sample interaction force is measured directly by the deflection of the cantilever and the feedback loop keeps the peak force constant during the photocurrent mappings, which enables direct, precise force control and eliminates lateral forces. According to the AFM results, the maximum depth of the cavities is ~ 180 nm, which is much less than the perovskite thickness (~ 380 nm), demonstrating that the CdS film was fully covered by the MAPbI₃ film. Therefore, we infer that the short transport distance of the cavity area from sample surface to the bottom of the MAPbI₃/CdS interface resulted in higher photocurrent value compared with the flat region (region 1). Previously, it was shown that excitons can separate more efficiently at the edges of a perovskite crystal, and the photogenerated carriers preferentially transport along its grain boundaries.^{60,61} It is therefore very likely that a similar process is at play here. The proposed transport mechanism of the photocarriers is illustrated in Figure 7g, where excitons preferentially separate at the grain boundaries of perovskite crystals and therefore the edges of the cavities exhibit higher photocurrent.

Spatial Analysis of Photocurrent Generation. Spatial analysis was performed on the topographic mapping and dark/photo current mappings to study the transport mechanism of photon-generated carriers. Figure S14a-c show the topographic, dark current and photocurrent images under 1.8 V. The 2D fast Fourier transforms (FFTs) were conducted on these three mappings as shown in Figure S14d-f. The center of the topographic FFTs image (Figure S14d) exhibits the strongest intensity. However, the intensity of dark current FFTs image (Figure S14e) shows a dispersed concentric feature. And it is very interesting that the intensity in the center of photocurrent FFTs image (Figure S14f) is slightly stronger than the dark current FFTs image. The FFTs analysis suggests that the photocurrent mapping exhibits closer relationship with the topographic mapping compared with dark current mapping. As mentioned above, excitons tend to separate more efficiently at the edges of a perovskite crystal, and then the carriers transport along the edges, so the photocurrent appeared stronger at grain boundaries of

the perovskite as shown in Figure S12, which makes the profile of perovskite crystal appear clearer. Thus, the closer relationship between the photocurrent FFTs image and topographic FFTs image further proves the photocurrent enhancement effect at grain boundaries.

Discussion the Effect of the Interfaces (Tip/MAPbI₃, CdS/ITO). In order to study the influence of the interfaces (tip/MAPbI₃ and CdS/ITO) on the charge carrier transport in tip/MAPbI₃/CdS/ITO system, the work function (WF) of CdS and MAPbI₃ were measured via Kelvin probe force microscopy (KPFM) as shown in Figure S15. The WF of the tip ($\Phi_{\text{tip}}=4.90$ eV) was calibrated against a graphite crystal (freshly peeled surface) and the WF of the sample was calculated using:

$$\Phi_{\text{sample}} = \Phi_{\text{tip}} - V_{\text{CPD}} \quad (9)$$

V_{CPD} is the potential difference between sample and tip, which can be obtained by analyzing the KPFM mapping.⁶¹ The WF of CdS and MAPbI₃ was determined to be 4.71 eV and 4.88 eV, respectively. Herein, the ITO electrode has a WF (Φ_{ITO}) of ~4.7 eV. Thus, the $\Phi_{\text{B,MAPbI}_3/\text{Tip}}$ ($\Phi_{\text{MAPbI}_3} - \Phi_{\text{Tip}}$) and $\Phi_{\text{B,CdS/ITO}}$ ($\Phi_{\text{CdS}} - \Phi_{\text{ITO}}$) is quite small, which makes the interfaces (tip/MAPbI₃, CdS/ITO) have very weak effect on the carrier transport.

CONCLUSION

In summary, we demonstrated MAPbI₃/CdS heterojunction photodetectors for the first time. The resulting devices exhibit excellent performance including high current on/off ratio $\sim 1.13 \times 10^5$, detectivity of $\sim 9.79 \times 10^{10}$ Jones and PCE of up to ~10.05%. Moreover, the mechanisms of photocurrent generation and transport across the MAPbI₃/CdS heterointerface have been studied down to nanoscales via C-AFM and PC-AFM. Obtained results demonstrated that the combination of CdS with MAPbI₃ lead to a remarkably improved photodetector performance, and lay the foundation for future work.

EXPERIMENTAL SECTION

Materials. Ammonium hydroxide, NH_4Cl , thiourea ($\text{SC}(\text{NH}_2)_2$), CdCl_2 , anhydrous dimethylsulfoxide (DMSO) and N,N-dimethylformamide (DMF) were purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD. Methylamine Hydroiodide (MAI) and PbI_2 were purchased from Xi'an Polymer Light Technology Corp, all the chemicals were used as received without further purification.

Device Fabrication. Through CBD method, the uniform film of CdS was fabricated on ITO substrates.⁶² The precursor solution including NH_4OH (0.640Mol/L), NH_4Cl (0.015Mol/L), thiourea ($\text{SC}(\text{NH}_2)_2$ (0.003Mol/L)), CdCl_2 (0.002Mol/L) and deionized water was prepared before deposition. Then the ITO substrate was placed in the solution vertically by a clamp as shown in Figure 1a. Solution bath system was kept magnetically stirred and the temperature was maintained at 80 °C by a hot plate. The deposition time was 5 min, 7 min, 9 min, 11 min and 13 min, respectively. After the CBD process, the backside of the ITO was treated by dilute hydrochloric acid, since the CdS on the backside can block the light path and decreased the PCE of $\text{MAPbI}_3/\text{CdS}$ photodetector. Then the CdS film was dipped in saturated CdCl_2 /methanol solution for 15 times. The deposited CdS was further gently washed by DI water. After that, thermal treatment was applied on the CdS thin film at 400 °C in Ar atmosphere for 20 min. The produced CdS thin film was characterized by Raman and XRD to confirm the successful synthesis.

The MAPbI_3 films were fabricated by a one-step-method.^{63,64} The MAPbI_3 precursors including 159 mg MAI and 461 mg PbI_2 were dissolved in 70 μL anhydrous DMSO and 630 μL DMF. Then 120 μL precursor solution was spun onto the CdS film at 2,500 rpm for 3 s and 4,500 rpm for 25 s, and 120 μL toluene was dropped on the sample at 10 s quickly during the spin-coating. After that, thermal treatment was applied on the sample at 82 °C for 25 min. Finally, the gold counter electrodes were deposited by thermal evaporation.

Characterizations. The PC-AFM and C-AFM experiments were carried out by BRUKER DIMENSION ICON multi-function atomic force microscope, as illustrated in Figure 7a. All images were scanned with an image resolution of 512×512 pixels. While, the C-AFM and PC-AFM measurement is taken by peak force TUNA mode that provides direct, precise force control and eliminate lateral force, enabling routine high sensitivity and high resolution current imaging. In this mode, the current measurement is taken when the tip is contact with the sample with a constant force (150 nN, the maximum force between the tip and sample) for particular scanning area. The laser (405 nm) purchased from Changchun New Industries Optoelectronics Technology Co. Ltd. was used as the illumination light source. NanoScope-Analysis software package was used to process AFM images and generate FFT images.

The noise current of the devices was measured using a lock-in amplifier (Stanford Research System, SR830). During the measurement, a grounded metal box was used to keep the device in dark and reduce the noise produced by the electromagnetic interference. The PCE shown in Figure 4f was obtained by Enlitech QE-R3011.

Raman and PL spectra were obtained by a Witec Alpha 300R system with a 532 nm laser. XRD measurements were carried out by Rigaku D/MAX-2500. SEM images were taken by a JEOL JSM 6700F field emission scanning electron microscope. The thickness of CdS and MAPbI₃ layer were determined by the cross section SEM image of the prepared thin film.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the

[ACS Publications website](#) at DOI:

Photograph of the photodetectors. SEM images of CdS film and MAPbI₃ film. I-V curves of the MAPbI₃/CdS heterojunction photodetector and the MAPbI₃-only photodetector. I-V curves of the CdS-only photodetector. Discussion of noise current and noise equivalent power.

Optimize the thickness of CdS and MAPbI₃ layers. Noise current spectra of MAPbI₃/CdS photodetector. Photocurrent, photoresponsivity and detectivity of the MAPbI₃/CdS photoconductor under 1.5 V. Detectivity of MAPbI₃/CdS based photodetector under light wavelength from 300 nm to 800 nm. Dark current mappings. Photocurrent mappings. Photoresponse mappings. Estimation of effective contact area. 2D FFTs images. Surface potential image.

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Notes

The authors declare no competing financial interest.

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