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High-Performance Planar-Type Ultraviolet Photodetector Based on High-Quality CH₃NH₃PbCl₃ Perovskite Single Crystals

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Supporting Information

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ABSTRACT: A hybrid perovskite MAPbCl₃ (MA = $CH_3NH_3^+$) single crystal is considered to be one of the most viable candidates for the development of photodetectors because of its outstanding optoelectronic properties. However, the relatively lower crystalline quality of the reported MAPbCl₃ single crystals fabricated by the traditional one-step inverse temperature crystallization results in momentous degradation in the performance of their photodetectors. Here, we present a novel two-step temperature process to fabricate high-quality MAPbCl₃ single crystals, namely, lower temperature nucleation and higher temperature crystallization. These MAPbCl₃ single crystals present low defect density (\sim 7.9 × 10^9 cm⁻³) commensurate with the best-quality crystals of hybrid organicinorganic lead halide perovskites reported so far. Moreover, a high-performance ultraviolet photodetector was demonstrated on MAPbCl₃ single crystals. At 30 V, the peak responsivity at 415 nm of the photodetector is as high as 3.73 A W^{-1} (light intensity = 1 mW cm⁻²), $\sim 2-3$ orders of magnitude higher than that of the



previously reported MAPbCl₃ photodetectors. Meanwhile, the device has an ultrafast response speed with a rise time of 130 ns, which is one of the shortest values of MAPbX₃-based photodetectors. Our findings open a new way to obtain high-quality perovskite single crystals and their high-performance photodetectors.

KEYWORDS: CH₃NH₃PbCl₃, perovskite, photodetectors, single crystals, high speed

1. INTRODUCTION

Hybrid organic-inorganic lead halide perovskites, MAPbX₃ $(MA = CH_3NH_3^+, X = Cl^-, Br^-, and I^-)$, have gained a lot of attention because of their outstanding optoelectronic properties, including high carrier mobilities, large light absorption coefficients, long carrier diffusion lengths, and direct band gaps.^{1–4} These merits make them ideal for the fabrication in optoelectronic devices, such as solar cells,⁵⁻⁷ light-emitting diodes,^{8,9} lasers, and photodetectors.¹⁰⁻¹⁶ Compared with polvcrystalline films and nanostructures, perovskite single crystals exhibit better intrinsic properties because of their fewer defects and grain boundaries.¹⁷⁻¹⁹ For example, the charge carrier lifetime in MAPbBr3 single crystals is around 357 ns but only 168 ns in polycrystalline thin films.²⁰ Meanwhile, the carrier diffusion length in MAPbI₃ single crystals (175 μ m) is about 2 orders of magnitude longer than that in polycrystalline thin films $(1 \ \mu m)$.²¹ In addition, fewer defects and grain boundaries in single crystals could postpone the performance degradation MAPbX₃ materials, which will be beneficial for practical applications.²² Therefore, more and

more attention has been focused on MAPbX3 single crystals and their optoelectronic devices.^{23–26}

MAPbCl₃, a wide band gap semiconductor in the MAPbX₃ family (the band gap energy: ~ 3.1 eV at room temperature), is regarded as an attractive candidate for ultraviolet (UV) photodetection.²⁷ In the past few years, high-quality and millimeter-sized MAPbCl₃ single crystals and the corresponding photodetectors have been successfully demonstrated.²⁸ However, the photoresponsivity for the reported MAPbCl₃ single-crystal photodetectors is still below 50 mA W⁻¹, which is 3-7 orders of magnitude lower than that of the MAPbBr₃ (more than 4000 A W^{-1})²⁹ and MAPbI₃ (953 A W^{-1})³⁰ single crystals. This lower responsivity can be attributed to the relatively higher trap density $(3.1 \times 10^{10} \text{ cm}^{-3})$ of the reported MAPbCl₃ single crystals fabricated by traditional inverse temperature crystallization. Therefore, it is urgent to obtain

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high-quality $MAPbCl_3$ single crystals for high-performance and stable photodetectors.

In this work, we developed a two-step temperature process to fabricate MAPbCl₃ single crystals, namely, lower temperature nucleation and higher temperature crystallization. MAPbCl₃ single crystal obtained by using this method shows excellent crystalline quality, with a full width at half maximum (fwhm) of the X-ray diffraction (XRD) peak of 0.0447° and a trap density of ~7.9 × 10⁹ cm⁻³. Moreover, the photodetector based on MAPbCl₃ single crystal has superior responsivity as high as 3.73 A W⁻¹, >100 times better than the previously reported MAPbCl₃ single crystal devices. Meanwhile, the rise time is only 130 ns, which is one of the shortest values of the photodetectors based on hybrid organic—inorganic lead halide perovskites to the best of our knowledge.^{25,31–33} Also, the device shows a long-term stability of over 50 days preserved in the atmosphere.

2. EXPERIMENTAL SECTION

2.1. Preparation of MAPbCl₃ Single Crystals. Figure 1a shows the growth process of MAPbCl₃ single crystals. Lead chloride (PbCl₂)



Figure 1. a) Schematic illustration of the crystal growth process. (b) Photograph taken from a MAPbCl₃ single crystal. (c) SEM images of MAPbCl₃ single crystal at different magnifications.

(1.3905 g, \geq 99.0%, Shanghai No. 4 Reagent & H.V. Chemical Limited Company) and methyl-ammonium chloride (MACl) (0.3375 g, 98%, Aladdin) with an equimolar ratio were dissolved in a mixed solvent of *N*,*N*-dimethylformamide and dimethyl sulfoxide at 1:1 (2.5:2.5 mL) by a volume ratio at room temperature. The solution

was then stirred until no reactant precursor existed. Subsequently, the solution was filtered by using the poly tetra fluoroethylene filter with 0.45 μ m pore size. To grow the MAPbCl₃ single crystals, we first poured the precursor solution into some vials (1.5 mL per vial) for 5 h, which were kept in an oil bath with a temperature of 45 °C. Subsequently, the temperature of the oil bath was quickly increased to 60 °C and maintained for ~8 h. Then, MAPbCl₃ single crystals with sizes of 3–6 mm were obtained. Notably, compared to the conventional one-step heating method,²⁸ this two-step temperature process can produce high-quality MAPbCl₃ single crystals with a lower defect density. Also, the low-temperature nucleation process at 45 °C should play a very important role for the high crystalline quality.

2.2. Fabrication of the Photodetector. To fabricate the photodetectors, a microwire with a diameter of 30 μ m was chosen as a shadow mask to define the shape of the electrodes (see Figure S1). Sequentially, 30 nm-thick Au electrodes were then deposited on the smooth surface of the MAPbCl₃ single crystal by a thermal evaporation method at room temperature. As a result, the metal–semiconductor–metal (MSM) photodetector based on MAPbCl₃ single crystal was realized with the distance of 30 μ m between two Au electrodes.

2.3. Characterization and Measurements of Materials and Devices. The surface morphology of the single crystal was measured by the scanning electron microscope (SEM) (Hitachi S-4800). The absorption spectrum was recorded using the UV-3101PC scanning spectrophotometer. The photoluminescence (PL) spectrum of the single crystal was measured at room temperature using a He–Cd laser (325 nm) as the light source. The crystal structural properties were characterized by XRD (Bruker D8 DISCOVER) with Cu as the radiation source ($\lambda = 1.541$ Å). *I–V* curves and current–time (*I–t*) curves were measured by using a semiconductor parameter analyzer (Keithley 2200). The spectral responses of the fabricated devices were measured using a 200 W UV-enhanced Xe lamp with a monochromator as the light source.

3. RESULTS AND DISCUSSION

Figure 1b is a photograph of the transparent and glossy MAPbCl₃ single crystal with a cuboid shape and typical dimensions of 3 mm \times 3 mm \times 2 mm. The SEM images of MAPbCl₃ single crystal are presented in Figure 1c. It can be seen that the surface of the sample is very flat and no apparent grain boundary could be found on the surface.

The crystallinity of the MAPbCl₃ single crystal was measured by high-resolution XRD. Figure 2a shows the XRD 2θ scan result on the largest face of the MAPbCl₃ single crystal. Very sharp peaks at 15.56°, 31.45°, and 48.03° correspond to the (100), (200), and (300) planes of the cubic MAPbCl₃ crystal structure, respectively. Also, no other peaks associated with MACl and PbCl₂ can be found. Further XRD patterns on the other faces of the crystal indicate that they also belong to the same family of {100} planes (see Figure S2). In addition,



Figure 2. (a) High-resolution XRD 2θ scan pattern on the largest face of the MAPbCl₃ single crystal. (b) X-ray rocking curve pattern of the (100) plane of the MAPbCl₃ single crystal. (c) I-V curve of MAPbCl₃ perovskite crystal.



Figure 3. (a) I-V curves of the detector in the dark condition and under illumination with 365 nm UV lamp. Inset: Schematic illustration of the device structure with an active area size of 30 μ m × 3 mm. (b) Absorption and PL spectra of MAPbCl₃ single crystal, and the inset shows the Tauc plot to calculate its band gap. (c–e) Spectral responsivity (*R*), EQE, and detectivity (*D**) of the device measured at different biases.

the lattice constant of this MAPbCl₃ single crystal was estimated to be 5.67 Å, which is in good agreement with that of the previously reported MAPbCl₃ single crystals.^{28,34,35} The (100) XRD peak was further measured using the X-ray rocking curve as shown in Figure 2b. The fwhm for the (100) diffraction peak of MAPbCl₃ single crystal is estimated to be only 0.0447°, illustrating the excellent crystalline quality. For all we know, the fwhm of 0.0447° is the narrowest value reported to date for the MAPbCl₃ single crystals,³⁴ demonstrating the benefits of the two-step temperature process.

Moreover, to estimate the trap state density (n_{trap}) in MAPbCl₃ single crystal, the MAPbCl₃ single crystal was sandwiched between two Pt electrodes to constitute a holeonly device, and its current–voltage (I-V) characteristic was investigated by the space-charge-limited current method as shown in Figure 2c. It is obvious that the dark I-V curve could be divided into three different regions. When the voltage is lower than 8.1 V (V_{TFL} : known as trap-filled limit voltage), the linear relationship between current and applied voltage suggests an Ohmic response. As the applied voltage exceeds V_{TFL} , the current shows a steep increase ($I \propto V^{n>3}$), indicating that the traps in the MAPbCl₃ single crystal are filled by the charge carriers.^{36,37} The value of V_{TFL} can be used to estimate the trap state density of the single crystal by the following equation.²⁸

$$V_{\rm TFL} = \frac{e n_{\rm trap} L^2}{2\varepsilon \varepsilon_0} \tag{1}$$

where *e* is the elementary charge, *L* is the thickness of the crystal, ε is the dielectric constant of MAPbCl₃($\varepsilon = 23.9$),²⁸ and ε_0 is the vacuum permittivity. Therefore, the trap state density in our sample can be obtained as ~7.9 × 10⁹ cm⁻³, significantly lower than that of the previously reported MAPbCl₃ single crystal (3.1 × 10¹⁰ cm⁻³).²⁸ When the bias is higher than 20 V, the current–voltage curve can be fitted by the Mott–Gurney law²⁸

$$J_{\rm d} = \frac{9\varepsilon\varepsilon_0\mu V^2}{8L^3} \tag{2}$$

where J_d is the dark current density, μ is the carrier mobility of the MAPbCl₃ single crystal, and *V* is applied bias, respectively. The carrier mobility μ in the MAPbCl₃ single crystal is up to ~64 cm² V⁻¹ s⁻¹, larger than the previously reported value.²⁸ These results prove again that we have obtained high-quality MAPbCl₃ single crystals with very low density of trap states, which are vital to the fabrication of high-performance optoelectronic devices.

To scrutinize the photoelectric properties of the MAPbCl₃ single crystal, we fabricated an MSM photodetector and the structure of the device is shown in the inset in Figure 3a. The I-V curves of the photodetector were tested both in dark and under light illumination of the 365 nm UV lamp (light density of 1 mW cm⁻²), as shown in Figure 3a. The dark current and photocurrent are 5.23×10^{-8} and 1.04×10^{-6} A at 15 V, respectively. The relatively low dark current can be attributed to the high-quality MAPbCl₃ single crystal. The responsivity (*R*) of the device is calculated using the following formula^{38,39}

$$R = \frac{I_{\text{light}} - I_{\text{dark}}}{P_{\text{light}} \times S}$$
(3)

where I_{light} and I_{dark} are the photocurrent and dark current, respectively. P_{light} is the irradiance power density and S is the illuminated active area of the device. The responsivity of the device was calculated to be 1.316 A W⁻¹ under the light density of 1 mW cm⁻² (365 nm) at 15 V.

The absorption and PL spectra of the MAPbCl₃ single crystal are shown in Figure 3b. Obviously, the absorption edge can be found at 428 nm, and the optical band gap can be obtained as 2.89 eV by plotting the Tauc plot (see the inset of Figure 3b). The sharp absorption edge implies a low concentration of in-gap trap states. In addition, a narrow fwhm of 11.8 nm for the PL peak at 405 nm reveals excellent crystalline quality. According to the previous reports, the blue-shift of the PL peak relative to the absorption edge can be explained as follows.^{21,40} There is strong excitonic absorption

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Figure 4. (a) 33 on–off switching circles of the photoresponse at the bias of 15 V under 365 nm UV illumination with different irradiance power densities. (b-d) Power-dependent responsivity, external quantum efficiency, detectivity of the device with the irradiance power densities changing from 0.09 to 1.53 mW cm⁻² using 365 nm UV light.



Figure 5. (a,b) Transient photocurrent response at the voltage of 15 V under 365 nm pulsed laser. The rise and fall time of the photodetector is obtained to be 130 ns and 368 μ s, respectively. (c) Long-term stability test of MAPbCl₃ single crystal-based photodetector under ambient conditions (temperature: 24–28 °C, relative humidity: 20–60%) without any encapsulation. The insets show the temporal photoresponse of the device after 3, 26, and 46 days storage.

in the MAPbCl₃ single crystal, causing a long-wavelength shift (redshift) of the absorption edge. Meanwhile, the exciton dissociates at room temperature. Therefore, an obvious anti-Stokes shift between the PL peak and the absorption edge can be observed in our MAPbCl₃ single crystal.

Figure 3c shows the responsivity spectra of the device under different applied voltages. It could be seen that the peak responsivity appears at the wavelength of 415 nm with the -3dB cut-off edge at around 420 nm. These results are consistent with the absorption spectrum in Figure 3b. Additionally, with increasing the applied bias from 10 to 30 V, the peak responsivity of the MAPbCl₃ single-crystal photodetector at 415 nm increases from 1.85 to 3.73 A W⁻¹. The external quantum efficiency (EQE) of the devices can be calculated by the following equation

$$EQE = \frac{R \times hc}{e\lambda}$$
(4)

where *R* is the responsivity of the device, *h* is the Planck's constant, *c* is the speed of light, and λ is the wavelength of

incident light. At the bias voltage of 30 V, the peak responsivity at 415 nm is up to 3.73 A W⁻¹ and the corresponding EQE is estimated to be 1115%, as shown in Figure 3c. Detectivity (D^*) is another important factor for photodetectors, which is given by the following equation⁴¹

$$D^* = \frac{\sqrt{A\Delta f R}}{i_n} \tag{5}$$

where A is the active area of the detector, Δf is the noise equivalent bandwidth, and i_n is the dark current. D^* can reach up to 9.97 × 10¹¹ Jones at 415 nm under 30 V bias, which is more than two orders of magnitude higher than that of the previously reported MAPbCl₃ photodetectors.²⁸

The on-off switching properties of the MAPbCl₃ singlecrystal photodetector are presented in Figure 4a. It is obvious that the device can be switched on and off repeatedly and stably with different irradiance power densities. Furthermore, Figure 4b-d shows the *R*, EQE, and D^* values as a function of the illumination intensity. It can be found that *R*, EQE, and D^*

Table 1. Comparison of t	he Critical Parameters	between this Work and	l Various MAPbCl ₃	, Photodetectors
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light absorber	fwhm of XRD peak (deg)	trap density (cm ⁻³)	responsivity	rise time (10–90%)	decay time (90–10%)	refs
MAPbCl ₃ crystals			$\sim 1 \text{ A W}^{-1}$ @385 nm, ($\sim 2 \text{ mW cm}^{-2}$) ^c		~1 ms	27
MAPbCl ₃ SC ^a		3.1×10^{10}	46.9 mA W ⁻¹ @365 nm	24 ms	62 ms	28
MAPbCl ₃ SC	0.11		0.62 mA W ⁻¹ @405 nm			34
MAPbCl ₃ PF ^b			0.97 A W ⁻¹ @360 nm, (2.2 mW cm ⁻²)	170 µs	220 µs	43
MAPbCl3 PF			71 mA W ⁻¹ @398 nm			46
MAPbCl ₃ SC	0.0447	7.9×10^{9}	3.73 A W^{-1} @415 nm, (1 mW cm ⁻²)	130 ns	368 µs	this work
^a SC is the abbrour	istion for single strated	^b DE is the ab	broviation for polycrystalling films. ^C Th	a irradianca navy	or donaitu ia calcu	lated by the

"SC is the abbreviation for single crystals. "PF is the abbreviation for polycrystalline films. "The irradiance power density is calculated by the following relation: $P_{opt}/A = P_{inc}/A_{dev}$ where P_{opt} is the optical power coming through the aperture, *A* is the aperture area, P_{inc} is the incident power, and A_{det} is the active area of the detector."

decrease almost linearly with increasing the illumination intensity. This phenomenon is in good agreement with the previous reports because of more carrier recombination happening under high light intensity.⁴² Consequently, *R*, EQE, and *D** values could reach as high as 2.27 A W⁻¹, 772%, and 6.07×10^{11} Jones, respectively, at 365 nm under 15 V bias with the illumination intensity of 0.09 mW cm⁻².

To further investigate the response speed and repeatability of the photodetector, the transient photoresponse was measured using a pulsed YAG:Nd laser (the laser pulse width was 10 ns and the frequency was 10 Hz) as shown in Figure 5a,b. The device shows excellent reproducibility and very fast response speed with a 10–90% rise time (t_{rise}) of 130 ns and a 90–10% fall time (t_{fall}) of 368 μ s. The rise time ($t_{rise} =$ 130 ns) is 3–5 orders of magnitude faster than that of almost all the reported MAPbX₃ photodetectors (only slower than that of the MAPbI₃-based photodetector reported by Huang et al.).^{28,30,43,44}

Long-term stability of the photodetector is another key parameter for practical applications.⁴⁵ In order to investigate the stability of the device, responsivity at 365 nm was periodically recorded for 53 days under ambient storage conditions (temperature: 24-28 °C, relative humidity: 20-60%) without any encapsulation, as shown in Figure 5c. It can be seen that the responsivity of the detector shows 24% degradation after 5 days. After that, responsivity decreases slowly and only 35% degradation can be observed after more than 50 days storage. Moreover, it can be seen in the insets of Figure 5c that the response speed of the detector shows no obvious degradation after 46 days of storage in the atmospheric environment. This excellent stability could be ascribed to the fewer defects and grain boundaries in our single crystal, making it very promising for practical applications.

The performance parameters of the reported MAPbCl₃ photodetectors based on both polycrystalline films and single crystals are summarized in Table 1. Note that our device has the highest responsivity among reported MAPbCl₃-based photodetectors. Both fwhm of the XRD peak and trap density of our MAPbCl₃ single crystal are lower than these of any previously reported MAPbCl₃ materials, which should be the main factor for the high performance of our device. Additionally, our single crystal photodetector has the shortest rise time among devices based on MAPbCl₃. By the comparison in Tables 1, S1, and S2, it can be concluded that MAPbCl₃ single crystal fabricated by two-step heating method possesses the better crystalline quality, lower trap density and higher photoresponse property.

4. CONCLUSIONS

In summary, we have developed a high-efficiency two-step crystallization method to fabricate high-quality MAPbCl₃ single crystals. The obtained MAPbCl₃ single crystals in this work present the narrowest fwhm of the XRD peak (~0.0447°), the largest carrier mobility (~64 cm² V⁻¹ s⁻¹), and the lowest trap state density ($\sim 7.9 \times 10^9$ cm⁻³) among the MAPbCl₃ materials reported so far. Moreover, the MAPbCl₃ single crystal photodetector has a high responsivity of 3.73 A W^{-1} at 415 nm and a rapid response speed with the rise time of 130 ns, which are much better than those of any previously reported MAPbCl₃ devices. In addition, this device shows long-term stability of over 50 days preserved in atmosphere without encapsulation. All these results indicate that the MAPbCl₃ single crystals prepared by our two-step temperature process should have great potential in high-performance optoelectronic devices, which will provide guidance for further research on perovskite photodetectors.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b09035.

Schematic of the fabrication process of the photodetector; high-resolution XRD 2θ scan; comparison of the property parameters of MAPbCl₃ single crystals obtained by the two-step and one-step methods; and comparison of the key performance parameter of photodetectors based on MAPbCl₃ single crystals obtained by the two-step and one-step methods (PDF)

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Author Contributions

The manuscript was written through contributions of all the authors. All the authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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