ACS APPLIED MATERIALS & INTERFACES

Chemical Vapor Deposition Method Grown All-Inorganic Perovskite **Microcrystals for Self-Powered Photodetectors**

Cancan Tian,^{†,‡} Fei Wang,^{*,†} Yunpeng Wang,[†] Zhe Yang,^{†,‡} Xuejiao Chen,^{†,‡} Jingjing Mei,^{†,‡} Hongzhen Liu,^{†,‡} and Dongxu Zhao*

[†]State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 3888 Dongnanhu Road, Changchun 130021, People's Republic of China

[‡]University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China

Supporting Information

ABSTRACT: Self-powered photodetectors (SPPDs) have attracted lots of attention due to their various advantages including no external power sources, high-sensitivity, fast response speed, and so on. This study reports the fabrication and characterization results of CsPbBr₃ microcrystals (MCs) grown by chemical vapor deposition (CVD) method, and the SPPDs have been fabricated on the basis of the CsPbBr₃ MCs layer with the sandwich structure of GaN/CsPbBr₃ MCs/ZnO. Such designed SPPD shows the detectivity (D^*) of 10^{14} Jones, on/off ratio of up to 10^5 , peak responsivity (R) of 89.5 mA/W, and enhanced stability at the incident wavelength of 540 nm. The photodetector enables the fast photoresponse speed of 100 μ s rise time and 140 µs decay time. The performances of the SPPD are



comparable to the best ones ever reported for CsPbBr₃ based PDs but do not need external power supplies, which mainly benefit from the low trap density, long carrier diffusion of high quality CsPbBr₃MCs film, and the built-in electric fields in the sandwich structure of GaN/CsPbBr₃/ZnO layers.

KEYWORDS: all-inorganic perovskites, CVD, photodiode photodetectors, self-powered photodetectors, CsPbBr₃ microcrystals

INTRODUCTION

Photodetectors (PDs), which can capture light signals and convert them into electric signals, have been widely used in various industrial and scientific applications including optical communication, imaging technique, environmental monitoring, optoelectronic circuit, security surveillance, and chemical/ biological sensing.¹⁻³ Capabilities the industrial applications require from the PDs are lower power consumption, higher responsivity, and faster response speed. However, conventional PDs are usually driven by external power sources such as batteries and direct-current power supplies, which have not only added extra cost, but also lead to serious environment problems. Therefore, self-powered photodetectors (SPPDs) have become more and more attractive in recent years due to their advantages of no power consumption.⁴ In general, SPPDs can be divided into two groups:⁵ one type is photoconductive devices, which can be driven by mechanical energy or chemical energy; another type is performed by exploiting photovoltaic effect (built-in electric field) from p-n junctions or Schottky junctions. Photoconductive PDs exhibit the high on/off ratio of photocurrent and dark current due to their large surface-area-tovolume ratio.^{6–8} However, the surface traps of photoconductive PDs result in long recovery time, which has seriously hindered their promising applications in high-speed optical communication and high-resolution imaging.⁹ In recent years, SPPDs with

the introduction of interface layers (hole- or electron-blocking layers) have shown fast response speed and high responsivity,^{2,10,11} which provide a better way to realize high performance PDs without energy consumption.

Owing to the outstanding optoelectronic properties such as ultrafast charge generation, high mobility, long charge carrier lifetime, etc.,¹² considerable attention has been attracted by hybrid organic-inorganic lead halide perovskites (ABX₃, A = $CH_3NH_3^+$, and X = Cl, Br or I) for various applications such as laser,^{13,14} light emitting diodes (LEDs),^{15,16} PDs,^{2,17,18} and especially solar cells.^{19,20} However, the instability of hybrid lead halide perovskites under moisture, heat, or strong light have severely limited their further applications in long-term device.^{21,22} To eliminate the barrier caused by instability for their applications, various routes were designed and experimentally operated; one of the most effective ways is substituting organic cations with inorganic cesium atoms.²³ Compared with organometal halide perovskites, cesium based all-inorganic perovskites exhibit better photostability; therefore, the bulk materials and the nanocrystal films of which have achieved increasing success in the field of PDs recently.²⁴⁻³⁶ In 2016,

Received: February 26, 2019 Accepted: April 9, 2019 Published: April 9, 2019



Figure 1. (a, b) Typical SEM images showing the morphology of CVD grown CsPbBr₃ MCs at low and high magnifications, respectively. (c) HRTEM results of CsPbBr₃ MC demonstrating the high crystalline quality with the lattice of 0.27 nm. (d) XRD spectrum indicating the orthorhombic structure of CsPbBr₃ MCs.

Zeng et al. fabricated the CsPbBr₃ films via centrifugal-casting method, after applying interdigitated Au as electrodes, the PD with the responsivity of 10.04 mA/W and the detectivity of 10⁸ was achieved.²⁴ Song et al. assembled flexible PDs on the synthesized high-quality 2D CsPbBr₃ nanosheets, which exhibited a high sensitivity of 0.64 A/W and a light on/off ratio of $10^{3.25}$ In the past few years, the PDs based on the different morphology of CsPbBr₃ such as nanocrystals (NCs),^{26–28} nanowires,²⁹ nanoplates,³⁰ and microcrystals (MCs)^{31,32} were constructed. Meanwhile, the PDs with different $(MCs)^{26,21}$ electrodes, such as Au,^{24,26,27} Pt,³⁵ ITO,^{25,31} and graphite,³ were also investigated. However, most reported CsPbBr₃ based PDs are photoconductive devices, which means they are still unable to drive themselves without external power sources. In 2017, Saidaminov et al. reported the CsPbBr₃ based SPPD with Pt and Au as electrodes.³⁵ Owing to the semimetal channel,²⁸ the rise and decay times of the SPPD were 230 and 60 ms, respectively, which are much slower than those of the photoconductive PDs. Therefore, the CsPbBr₃ based SPPDs with high response and fast speed are needed. GaN and ZnO, which have been wildly exploited in optoelectronic field,^{37,38} have outstanding optical and electrical properties. Moreover, their broad bandgap of above 3.0 eV and high melting point will not affect the absorption of CsPbBr3 material but enhance the stability of the perovskites-based devices. Thus, for all the above reasons, p-GaN and n-ZnO are the excellent charge transport layers for CsPbBr₃ to realize high performance SPPDs.

Generally, the SPPDs contain the photodiode structure of thin films, which require the facile and low-cost growth technique for mass production. CVD method is wildly used for the growth of semiconductor films in industry today. Compared to the solution method, the sealed and solvent free environment of CVD technique during the growth process could avoid the formation of gain boundary, surface defects and groups in as-grown materials, which could effectively enhance the carriers transport characteristic and chemical stability of thin films. Therefore, in this work, we have developed a direct growth approach of CsPbBr₃ MCs film on p-type GaN substrate by CVD method, and SPPDs of high performance were achieved on the basis of the MCs film. It is well-known that the film quality will strongly affect the performances of the PDs. Direct CVD growth of CsPbBr3 materials on an inorganic charge transport layer is a feasible path to fabricate dense, uniform, and crack-free films, which could also avoid the surface defects and grain boundaries in the solution-processed films. The GaN substrate was uniformly covered by the CsPbBr3 MCs film with the thickness of about 2 μ m. X-ray diffraction (XRD) and transmission electron microscope (TEM) spectra indicate the high crystallinity of CsPbBr₃ MCs. The SPPD was fabricated by spin-coating n-type ZnO nanoparticles on the top of as-prepared CsPbBr₃ MCs film. Meanwhile, the p-type GaN and n-type ZnO layers are the electrons and holes blocking layers as well. The device presented high detectivity, high on/off ratio, fast photoresponse speed, and enhanced stability at 0 bias voltage. The performance of the SPPD can be ascribed to the high quality CsPbBr₃ MCs and the sandwich structure of the device, which takes the advantages of charge blocking layers and built-in fields of junctions.

RESULTS AND DISCUSSION

Figure 1a and b show the SEM images of CsPbBr₃ MCs. As can be seen from the pictures, the MCs present the shape of quadrate, and the size of the MCs is approximately 12 μ m. The HRTEM image (Figure 1c) reveals the high crystalline quality of CsPbBr₃ MC with the lattice of 0.27 nm, which is in accord with the atomic model of the CsPbBr₃ shown in the inset of Figure S1. Also, the XRD pattern shown in Figure 1d indicates that the crystals belong to orthorhombic CsPbBr₃^{31,35} and the narrow



Figure 2. Optical properties of the CsPbBr₃ MCs. (a) Steady-state absorption spectrum, the absorption edge was determined by using Tauc plot. (b) Steady-state PL spectrum ($\lambda_{ex} = 360$ nm). (c) Steady-state PL spectrum pumped by femtosecond laser of 800 nm. (d) PL spectra of an individual crystal under different pump powers.



Figure 3. (a) Fabricating diagram of the CsPbBr₃ MCs based SPPD. (b) Cross-sectional SEM image of the device and the EDX spectrum of CsPbBr₃ MCs film.

full-width at haft-maximum (fwhm) of the peaks confirms the high purity of the crystals.

For further revealing the quality of the CsPbBr₃ MCs, the optical properties of the sample were investigated and shown in Figure 2. The sharp absorption edge of CsPbBr₃ MCs in Figure 2a is located at 546 nm, which corresponds to the bandgap of

2.27 eV (insert of Figure 2a). One photon and two photons absorption induced photoluminescence (PL) spectra are demonstrated in Figure 2b and c, respectively. Under the illumination of 360 nm (one photon excitation), two emission peaks can be found at the wavelengths of 520 and 550 nm. The same phenomenon has also been observed in previous



Figure 4. (a) I-V characteristics of the device in dark and under the 540 nm illumination of 3.5×10^{-3} W cm⁻². (b) Room temperature spectral responsivity curves of the device at 0 V bias.

reports.^{31,39,40} However, the origination of the peak at 520 nm (2.38 eV) is still unclear. Sebastian et al. ascribed the abovebandgap emission to Br vacancies on the basis of the density functional theory calculations.³⁹ Saouma et al. confirmed the existence of the energy level by using wavelength-dependent multiphoton absorption spectroscopy.⁴⁰ Also, Yang et al. considered the PL peak at 520 nm is the result of the carriers' recombination emission on the surface of the MCs.³¹ While pumped by femtosecond laser of 800 nm (two photons excitation), only one peak at 553 nm can be observed without any spectral shift. In this case, the photoinduced carriers are generated in the whole MCs, the carriers' recombination emission on the surface is negligible in the spectrum. Obviously, the PL peak at 550 nm (2.25 eV) originates from quasibandedge emission, and the tiny difference between 550 and 553 nm can be ascribed to the Burstein-Moss effect.³¹ Additionally, there are also several secondary interference fringes that can be attributed to the presence of high reflective surfaces of CsPbBr₃ MCs. Room temperature lasing characteristics of MCs were performed and shown in Figure 2d. For an individual CsPbBr₃ crystal, a sharp peak with the fwhm of less than 0.5 nm was observed with the pumping energy of 5.35 μ W. When the pumping power increased to 5.8 μ W, more sharp peaks were appeared. Figure S2 shows the plots of the PL peak intensity versus pumping power, the PL intensity increased rapidly with the further increasing pumping energy and the lasing threshold was found to be 6.6 μ W. The lasing phenomenon indicates the good morphology, high crystal quality, and low defect density of CsPbBr₃MCs. Also, the tolerance of high pumping energy manifests the robustness of the MCs as well.

The appealing properties of CsPbBr₃ include the low trap density and long carrier diffusion length, which are suitable for high performance PDs.^{31,35,41} Figure 3a shows the fabrication process of the SPPD based on CsPbBr₃ MCs. The CsPbBr₃ MCs film was sandwiched between p-GaN (hole-traport material, electron-blocking layer) and n-ZnO (electron-transport material, hole-blocking layer). Au was used as the top electrode, and Ni/Au was the back electrode. The detailed fabrication process is presented in the Materials and Methods. The morphology of CVD grown CsPbBr₃ MCs can be changed by the different temperatures and pressures in the furnace chamber. With the growth temperature of 580 °C, the size of CsPbBr₃ MCs increases to about 30 μ m, and the crystals are arranged disorderly (shown in Figure S3a). This is because the vapor of the reactant source tends to react and deposit on the low temperature substrates. The enhanced deposition of CsPbBr₃ results in the larger crystal size and irregular morphology. In contrast, when the deposition reaction is performed under high

temperature of 620 °C, the vapor of the reactant source can hardly deposit on the substrate, which results in the few and small crystals on the substrate in Figure S3b. The growth pressure was modulated from 150 to 200 Pa to accomplish the conversion from individual CsPbBr₃ MCs to CsPbBr₃ MCs film by changing Ar flow. Figure S4a shows the SEM image of CsPbBr₃ MCs film by the CVD pressure of 200 Pa with the corresponding Ar flow of 300 sccm. Figure S4b presents the device's sandwich structure by SEM. As shown in the picture, the GaN substrate has been wholly and uniformly covered by CsPbBr₃ MCs film without any pinholes, and the thickness of CsPbBr₃ MCs layer is approximately 2 μ m. The cross-sectional view of the device confirms that the interfaces between different layers are uniform and smooth (shown in Figure 3b). The right image of Figure 3b presents the EDX results of the MCs film, which shows the molar ratio of 1:1:3 (Cs:Pb:Br) with considering the deviation of the measurements.

Figure 4 presents the I-V measurements and photoresponsivity of the SPPD based on CsPbBr₃ MCs. The dark current curve of the device indicates the standard properties of p-n junction in Figure 4a (inset). The I-V curves of ZnO layer with Au as electrodes and GaN layer with Ni/Au as electrodes are shown in Figure S5, which indicate the formation of ohmic contacts between semiconductor layers (GaN and ZnO) and metal electrodes. Under the illumination of 540 nm light source (power density of 3.5×10^{-3} W/cm²), the strong photogenerated potential field has eliminated the barrier of junction and then resulted in the near-linear relationship of I-Vcharacteristics. The photocurrent has increased by five orders of magnitude versus dark current at 0 V bias, and the opencircuit voltage (V_{oc}) is 0.2 V. For a PD, responsivity (R) is defined as the ratio of photocurrent density and incident light intensity, which indicates how efficiently the detector responds to an optical signal. It can be expressed as

$$R = \frac{I_{\rm ph}}{L_{\rm light}} \tag{1}$$

where $I_{\rm ph}$ is the photocurrent and $L_{\rm light}$ is the power of incident light. The calculated responsivity of CsPbBr₃ MCs based SPPD is 89.5 mA/W, which is comparable to the previously reported perovskite PDs with metal—semiconductor—metal structure. We ascribe the high responsivity to the large absorption coefficient, high carrier mobility, and low trap-state density of high quality CsPbBr₃ MCs layer. To characterize the weakest level of light that the detector can operate, detectivity (D^*) is determined by the responsivity and the dark current. D^* can be given by



Figure 5. (a) Reproducible on/off switching of the device upon various light intensities with a 10 s cycle illumination at the bias of 0 V. (b) Power dependent responsivity and photocurrent of the device. (c) Power dependent detectivity and EQE of the device. (d) Response of the device to pulsed light irradiation at frequencies of 800 Hz.

device structure	configurations	responsivity (mA W ⁻¹)	detectivity (Jones)	on/off ratio	rise/decay time (ms)	source power (V)	ref
Au/NCs/Au	photoconduction	10.04	4.56×10^{8}	10 ⁶	0.2/1.2	2	24
ITO/nanosheets/ITO	photoconduction	640		10 ⁴	0.019/0.024	5	25
Au/NCs-TiO ₂ /Au	photoconduction	24 500	8.9×10^{13}	105	4700/2300	2	26
Au/thinfilm/Au	photoconduction	55 000	0.9×10^{13}	105	0.43/0.318	6	27
Au/NCs-MoS ₂ /Au	photoconduction	440	2.5×10^{10}	10 ⁴	0.72/1.01	10	28
Au/nanowires/Au	photoconduction	4400			0.252/0.3	1	29
Au/nanoplates/Au	photoconduction	34	7.5×10^{12}	10 ³	0.6/0.9	1.5	30
ITO/MCs/ITO	photoconduction	6×10^{4}	10 ¹³		0.5/1.6	3	31
graphite/2D-MCs/graphite	photoconduction	2100		10 ²	0.25/0.45	9	32
Au/thinfilm/Au	photoconduction	375	2.96×10^{11}	10	0.28/0.64	5	33
Au/thinfilm-ZnO/Au	photoconduction	4250		10^{4}	0.21/0.24	10	34
Pt/SC/Au	photodiode	28	1.7×10^{11}	10 ⁵	230/60	0	35
Au/SC/Au	photoconduction	2000		10 ³	0.069/0.261	5	36
SpiroOMeTAD/MCs/SnO ₂	photodiode	172	4.8×10^{12}	105	0.14/0.12	0	47
PTAA/MCs/SnO ₂	photodiode	206	7.23×10^{12}	10 ⁶	0.3/0.39	0	48
Au/MCs/Au	photoconduction	1330	8.6×10^{11}	10 ³	20.9/24.6	5	49
GaN/MCs/ZnO	photodiode	89.5	1.03×10^{14}	10 ⁵	0.1/0.14	0	this work

Table 1. Performance Parameters Based on CsPbB	SC Photodetectors Previously	y Reported and in This Work
--	------------------------------	-----------------------------

$$D^* = \sqrt{\frac{A}{2qI_{\rm D}}}R\tag{2}$$

where I_D is the dark current, q is the elementary charge, and the effective area A is 1 mm². The low dark current of 10 pA at 0 V bias determines the detectivity of the device could reach up to 10^{14} Jones (Jones = cm Hz^{1/2} W⁻¹), which results from the suppression of leak current by charge blocking layer. The ultralow dark current also displays the long-time stability in Figure S6.

Figure 4b presents the spectral photoresponse of the PD from 300 to 650 nm. It is known that the responsivity origins from the generation of photoexcited electron—hole pairs when the photon energy of incident light beyond the bandgap of the semiconductor material. There are several features indicated in

Figure 4b: (1) the responsivity decreases dramatically at 550 nm, which is in accordance with the absorption edge of 546 nm; (2) the peak of responsivity at 540 nm matches well with the bandgap of CsPbBr₃ MCs; (3) the broad range of sensitive wavelength from 360 to 550 nm demonstrates the detector has broad spectral photoresponse from UV to visible light. The responsivity at each wavelength from 360 to 550 nm maintains the relative high value of at least 28 mA/W, which indicates that the device also has good performance when the incident light varies from UV to visible light. Meanwhile, the responsivity decreases dramatically at nearly 525 nm, which is attributed to the exciton absorption tail at the wavelength of 540 nm. Previous reports also displayed the same character.^{42,43} In addition, the responsivity of the device in UV region derives from photogenerated electron–hole pairs in CsPbBr₃ MCs together

ACS Applied Materials & Interfaces

with those in p-GaN and n-ZnO layers at the same time. As a comparison, the spectral responsivity of the PD without perovskite layer has also been recorded and shown in Figure S7. The responsivity only covers the UV region and be cut off at 375 nm, which indicates the significance of perovskite MCs layer for the photodetection in visible light region.

The response time of device at 0 V bias was measured with the commercial light-emitting diodes (540 nm) as the light source by using a chopper to turn on/off the beam illuminated on the device (shown in Figure S8). Successive on/off switching tests of the device upon different light irradiation without external power are presented in Figure 5a, and the performance of detector does not display any obvious degradation in switching experiment. For a high performance PD, the ability to detect light over a wide intensity range is required. The powerdependent photocurrent curve presents the linear relationship between photocurrent and illumination power under the luminous intensities ranging from 4.41×10^{-5} to 3.5×10^{-3} W cm⁻² in Figure 5b. Because of the full light absorption of $CsPbBr_3$ layer with the microlevel thickness, the calculated R maintains the relative constant value with the change of light intensity in Figure 5b. The highest values of D^* and EQE could reach up to 10¹⁴ Jones and 20% as plotted in Figure 5c, respectively. Furthermore, the performance of the device has no tendency to deteriorate after being exposed to ambient air for 3 months (Figure S9), the photocurrent decays only by less than 5%. These optoelectronic properties have confirmed the promising application of the device as high performance SPPD.

Figure 5d shows that the rise time of current from 10% to 90% is approximately 100 μ s and the decay time from 90% to 10% is approximately 140 μ s. For comparison, some previously reported PDs of CsPbBr₃ are listed in Table 1. This rapid response speed manifests the fast separation and efficient extraction of photogenerated electron—hole pairs in the device, which can be mainly ascribed to the built-in fields at the interfaces between GaN/ZnO and CsPbBr₃ MCs film. To investigate the mechanism of the charge injection and separation behaviors in the device, time-resolved photoluminescence (TRPL) was carried out to measure the lifetime of carriers in CsPbBr₃, GaN/CsPbBr₃, and GaN/CsPbBr₃/ZnO (Figure 6). The measured 540 nm PL decay times and amplitudes can be obtained by fitting TRPL decay curves with biexponential formula



Figure 6. TRPL spectra of CsPbBr₃,GaN/CsPbBr₃, and GaN/CsPbBr₃/ZnO, respectively.

$$f(t) = A + B_1 \exp\left(-\frac{t}{\tau_1}\right) + B_2 \exp\left(-\frac{t}{\tau_2}\right)$$
(3)

where *A*, *B*₁ (*B*₂), and τ_1 (τ_2) are constant, the decay amplitudes and decay times, respectively. As listed in Table 2, the PL decay

 Table 2. Fitting Parameters of TRPL Spectroscopy Based on

 Samples with Different Structure

samples	$ au_1$ (ns)	% of $ au_1$	τ_2 (ns)	% of τ_2	$ au_{\mathrm{ave}}\left(\mathrm{ns} ight)$
CsPbBr ₃	73.62	73.83	164.3	26.17	97.35
GaN/CsPbBr ₃	31.54	82.84	257.4	17.16	70.30
GaN/CsPbBr ₃ /ZnO	11.15	89.62	154.7	10.38	26.04

times of CsPbBr₃ MC τ_1 = 73.62 ns (B₁: 73.83%) and τ_2 = 164.3 ns (B₂: 26.17%), respectively. In comparison, when CsPbBr₃ MCs layer was growth on p-type GaN substrate, τ_1 decreased to 31.54 ns (B₁: 82.84%) and τ_2 increased to 257.4 ns (B₂: 17.16%). Furthermore, after coating ZnO layer on the top of CsPbBr₃ MCs layer, τ_1 and τ_2 were further reduced to 11.15 ns (B₁: 89.62%) and 154.7 ns (B₂: 10.38%), respectively. The average decay time (τ_{ave}) can be defined as (ref 45)

$$\tau_{\rm ave} = \sum B_i \tau_i \tag{4}$$

As shown in Table 2, the τ_{ave} of CsPbBr₃ was significantly reduced from 97.35 to 26.04 ns when ZnO was coated onto GaN/CsPbBr₃. We can assume that the charges in CsPbBr₃ decay only by radiative relaxation or transfer through GaN and ZnO. The charge-transfer rate constant can be described as (ref 46)

$$k_{\rm et} = \frac{1}{\tau_{\rm ave-sandwich}} - \frac{1}{\tau_{\rm ave-perovskite}}$$
(5)

According to the values of Table 2, the charge-transfer rate constant is calculated to be 28.07 μ s⁻¹, and the corresponding charge-transfer time is 35.63 ns. These results indicate that introducing the sandwich structure (GaN/CsPbBr₃/ZnO) is an effective path to achieve faster charge transport at the interfaces of p-GaN/CsPbBr₃ and n-ZnO/CsPbBr₃.

For clear illustration, the energy band diagram of the device is shown in Figure 7. Under the illumination of 540 nm (beyond



Figure 7. Energy band diagram of the SPPD under the illumination of incident light at 0 V bias.



Figure 8. (a) On/off switch tests of SPPD under different temperature. (b) Temperature-dependent dark current (black line) and photocurrent (blue line).

the bandgap), the photon can stimulate electrons from the valence band to the conduction band in $CsPbBr_3 MCs$ film. The photoexcited electrons and holes spread to the interfaces of n-ZnO/CsPbBr_3 MCs and p-GaN/CsPbBr_3 MCs, respectively. Then they are swept quickly to charge transporting layers because of the built-in fields. After turning off the incident light, the built-in field sweeps the rest of photogenerated carriers and results in the rapid current attenuation.

It is well-known that the stability improvement of the perovskite-based devices is still a challenging issue. For revealing the thermal stability of our device, the performance of SPPD under the temperature of 298 K, 323 K, 353 K, 373 K, 383 K was measured, respectively. As shown in Figure 8a, we can observe that the photocurrent increases with the increasing of ambient temperature. The increased photocurrent stems from the ion migration.⁴⁹ The conductance of material is enhanced with the increasing temperature; meanwhile, the thermal energy exceeds the activation energy of Br-. Consequently, both photo- and dark currents show the positive correlation with operating temperature. As displayed in Figure 8b, it can be seen that the photocurrent increases from 3.4 μ A at 298 K to 5.0 μ A at 383 K. Also, the dark current shows the same tendency from 10 pA to 60 pA. Obviously, the increase rate of dark current is faster than that of photocurrent, resulting in the reduction of on/off ratio $(I_{\rm ph}/I_{\rm D})$ from 3.4 × 10⁵ to 8.2 × 10⁴ (shown in Figure S10a). Additionally, the crystal structure CsPbBr₃ would transform from orthorhombic to tetragonal at 362 K,⁵⁰ which results in the different curve shape of the photocurrent in Figure 8a. When the temperature is less than 363 K, the photocurrent gradually increases to the definite value after the incident light is turned on. Conversely, with the temperature over 363 K, the photocurrent immediately reaches to the maximum value then followed by slow decay. Furthermore, the device shows the recoverable temperature-dependent photocurrent, after cooling to room temperature, the photocurrent could recover to 95% of initial value in Figure S10b, which indicate that the device has the better tolerance to high temperature.

CONCLUSION

In summary, CsPbBr₃ MCs films were directly grown on p-type GaN substrate by CVD method and high performance SPPDs based on p-GaN/CsPbBr₃ MCs/n-ZnO sandwich structure were achieved. The TRPL spectra proved that the introduction of ZnO and GaN layers has sped up the charge transporting rate of CsPbBr₃. The device has not only shown high responsivity and detectivity of 89.5 mA/W and 10¹⁴ Jones, but also presented fast response speed of 100 μ s at 0 V bias voltage and enhanced stability. The high performance of the SPPD can be ascribed to

the high quality CsPbBr₃ MCs and the sandwich structure of the device, which takes advantages of charge blocking layers and strong built-in fields of junctions.

MATERIALS AND METHODS

Materials. $PbBr_2$ (99.0%), CsBr (99.9% metals basis), tetramethylammonium hydroxide (98%), dimethyl sulfoxide (DMSO, HPLC grade), and ethyl acetate (HPLC grade) were purchased from Aladdin Reagents. Zinc acetate hydrate (99.99% trace metals basis) was purchased from Sigma-Aldrich. Ethanol (>99%) and ethanolamine (>99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. p-GaN film was growth on the sapphire substrate by metal organic chemical vapor deposition (MOCVD) method.

Synthesis of ZnO Nanoparticles. ZnO nanoparticles were synthesized by the room temperature solution-percipitation method.⁴⁴ Briefly, the ethanol solution (10 mL) of tetramethylammonium hydroxide (5.5 mmol) and the DMSO solution (30 mL) of zinc acetate hydrate (3 mmol) were mixed together and the mixture was stirred for 24 h under ambient conditions. After being washed by adding ethyl acetate, ZnO nanoparticles were redispersed in ethanol and the process was repeated for three times. Additional ethanolamine (10 μ L) was conducted to stabilize the nanoparticles if necessarily.

Synthesis of CsPbBr₃ MCs Film. The CsPbBr₃ MCs film was grown by one-step CVD method in vacuum ambiance. p-type GaN film $(10 \text{ mm} \times 10 \text{ mm})$ was placed downstream of the quartz tube in the furnace. CsBr₂ and PbBr powder were thoroughly mixed with a molar ratio of 2:1 and then put into an alumina boat to act as the reactant source. Before the experiment, the GaN substrates were orderly ultrasonicated in acetone, ethanol, and deionized water (18 M Ω) for 10 min at room temperature, respectively. The distance between source boat and GaN substrate was 12 cm. Prior to heating, the quartz tube was pumped down to 150 Pa and followed by the flow of high-purity Ar (99.999%). For the growth of individual MCs, the flow rate of Ar was kept at 150 sccm; however, for the dense MCs films, the flow rate was optimized to 300 sccm. Then the furnace was heated to 600 °C at the temperature gradient of 20 °C per min and maintained for 15 min. After naturally cooled to room temperature, the CsPbBr₃ MCs film was grown on the GaN wafer.

Fabrication of SPPDs. The sandwich architecture of the SPPD is shown in Figure 3b. A thin layer of prepared ZnO nanoparticles was deposited onto the CsPbBr₃ MCs surface by spin coating at 2000 rpm for 45 s. After being annealed at 60 °C for 30 min, the substrates were transferred into vacuum thermal evaporation system. The 100 nm Ni/Au and 80 nm Au films as the electrodes were thermal evaporated on the GaN and ZnO layers under vacuum at a pressure of 2×10^{-3} Pa, respectively. The active area of film was measured to be about 1 mm².

Characterization. The XRD characterization was performed on a Bruker D8 system using Cu K α radiation. The morphology and components of the sample were testified by field emission scanning electron microscopy (FESEM) equipped with energy-dispersive X-ray spectroscopy (EDX). High-resolution transmission electron microscopy (HRTEM) spectra of the sample were obtained by Tecnai G2 F20 S-TWIN. The absorption spectrum was conducted by a Shimazu UV-

ACS Applied Materials & Interfaces

3101 PC spectrophotometer. The room temperature photoluminescence (PL) spectra of CsPbBr₃ MC were performed by an ACTON SpectraPro 2300i spectrograph and a Newport Ti:sapphire femtosecond with 35 fs pulse-width, 1 kHz repetition frequency, 800 nm center wavelength with an optical parametrical amplifier used to tune the output wavelength to 360 nm. Time-resolved PL spectra were obtained on an Edinburgh FLS 920 fluorescence spectrometer by using the pump beam of 405 nm laser. The I-V characteristics were measured by an Agilent B1500A semiconductor device analyzer. The timeresolved photoresponse curves of the device were measured by using a chopper to turn on/off the commercial light-emitting diodes (540 nm) that illuminated on the device. Spectra dependent photoresponse of the device were carried out by a detector system from Zolix Instruments with a Si photodetector as reference.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b03551.

Laser properties of CsPbBr₃ microcube, SEM image of CsPbBr₃ MCs films grown under different temperatures, I-V characteristics of ZnO layer and GaN wafer with mental electrodes, image of response time testing, time-stability tests of SPPD, and temperature-tolerance of SPPD (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: wangf@ciomp.ac.cn. Phone: +86-431-86708227. *E-mail: zhaodx@ciomp.ac.cn.

ORCID 0

Cancan Tian: 0000-0001-6510-3789 Hongzhen Liu: 0000-0001-6364-9403

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China under Grant Nos. 11874351, 11504367, 11874352, and 61805237 and the Research Foundation of Jilin province under Grant No. 20180519004JH.

REFERENCES

(1) Assefa, S.; Xia, F. N.; Vlaso, Y. A. Reinventing Germanium Avalanche Photodetector for Nanophotonic On-Chip Optical Interconnects. *Nature* **2010**, *464*, 80.

(2) Dou, L. T.; Yang, Y.; You, J. B.; Hong, Z. R.; Chang, W. H.; Li, G.; Yang, Y. Solution-Processed Hybrid Perovskite Photodetectors with High Detectivity. *Nat. Commun.* **2014**, *5*, 5404.

(3) Hu, X.; Zhang, X. D.; Liang, L.; Bao, J.; Li, S.; Yang, W. L.; Xie, Y. High-Performance Flexible Broadband Photodetector Based on Organolead Halide Perovskite. *Adv. Funct. Mater.* **2014**, *24*, 7373–7380.

(4) Su, L.; Zhao, Z. X.; Li, H. Y.; Yuan, J.; Wang, Z. L.; Cao, G. Z.; Zhu, G. High-Performance Organolead Halide Perovskite-Based Self-Powered Triboelectric Photodetector. *ACS Nano* **2015**, *9*, 11310–11316.

(5) Chen, H. Y.; Liu, K. W.; Hu, L. F.; Al-Ghamdi, A. A.; Fang, X. S. New Concept Ultraviolet Photodetectors. *Mater. Today* **2015**, *18*, 493.

(6) Wang, F.; Mei, J. J.; Wang, Y. P.; Zhang, L. G.; Zhao, H. F.; Zhao, D. X. Fast Photoconductive Response in Organometal Halide Perovskite Photodetectors. *ACS Appl. Mater. Interfaces* **2016**, *8*, 2840–2846.

(7) Nasiri, N.; Bo, R. H.; Wang, F.; Fu, L.; Tricoli, A. Ultraporous Electron-Depleted ZnO Nanoparticle Networks for Highly Sensitive Portable Visible-Blind UV Photodetectors. *Adv. Mater.* **2015**, *27*, 4336.

(8) Bo, R. H.; Nasiri, N.; Chen, H. J.; Caputo, D.; Fu, L.; Tricoli, A. Low-Voltage High-Performance UV Photodetectoes: An Interplay between Grain Boundaries and Debye Length. *ACS Appl. Mater. Interfaces* **201***7*, *9*, 2606.

(9) Wang, H.; Kim, D. H. Perovskite-Based Photodetectors: Materials and Devices. *Chem. Soc. Rev.* **2017**, *46*, 5204–5236.

(10) Su, L. X.; Yang, W.; Cai, J.; Chen, H. Y.; Fang, X. S. Self-Powered Ultraviolet Photodetectors Driven by Built-In Electric Field. *Small* **2017**, *13* (1701687), 9.

(11) Zhao, B.; Wang, F.; Chen, H. Y.; Zheng, L. X.; Su, L. X.; Zhao, D. X.; Fang, X. S. An Ultrahigh Responsivity (9.7 mAW⁻¹) Self-Powered Solar-Blind Photodetector Based on Individual ZnO-Ga₂O₃ Heterostructures. *Adv. Funct. Mater.* **2017**, *27* (1700264), 8.

(12) Ponseca, J. C. S.; Savenije, T. J.; Abdellah, M.; Zheng, K.; Yartsev, A.; Pascher, T.; Harlang, T.; Chabera, P.; Pullerits, T.; Stepanov, A.; Wolf, J. P.; Sundström, V. Organometal Halide Perovskite Solar Cell Materials Rationalized: Ultrafast Charge Generation, High and Microsecond-Long Balanced Mobilities, and Slow Recombination. J. Am. Chem. Soc. **2014**, *136*, 5189–5192.

(13) Zhu, H. M.; Fu, Y. P.; Meng, F.; Wu, X. X.; Gong, Z. Z.; Ding, Q.; Gustafsson, M. V.; Trinh, M. T.; Jin, S.; Zhu, X. Y. Lead Halide Perovskite Nanowire Lasers with Low Lasing Thresholds and High Quality Factors. *Nat. Mater.* **2015**, *14*, 636–642.

(14) Fu, A.; Yang, P. D. Lower Threshold for Nanowires Lasers. *Nat. Mater.* **2015**, *14*, 557–558.

(15) Tan, Z. K.; Moghaddam, R. S.; Lai, M. L.; Docampo, P.; Higler, R.; Deschler, F.; Price, M.; Sadhanala, A.; Pazos, L. M.; Credgington, D.; Hanusch, F.; Bein, T.; Snaith, H. J.; Friend, R. H. Bright Light-Emitting Diodes Based on Organometal Halide Perovskite. *Nat. Nanotechnol.* **2014**, *9*, 687.

(16) Kim, Y. H.; Cho, H. C.; Heo, J. H.; Kim, T. S.; Myoung, N. S.; Lee, C. L.; Im, S. H.; Lee, T. W. Multicolored Organic/Inorganic Hybrid Perovskite Light-Emitting Diodes. *Adv. Mater.* **2015**, *27*, 1248– 1254.

(17) Wei, H. T.; Fang, Y. J.; Mulligan, P.; Chuirazzi, W.; Fang, H. H.; Wang, C. C.; Ecker, B. R.; Gao, Y. L.; Loi, M. A.; Cao, L.; Huang, J. S. Sensitive X-ray Detectors Made of Methylammonium Lead Tribromide Perovskite Single Crystals. *Nat. Photonics* **2016**, *10*, 333.

(18) Dong, R.; Fang, Y. J.; Chae, J. S.; Dai, J.; Xiao, Z. J.; Dong, Q. F.; Yuan, Y. B.; Centrone, A.; Zeng, X. C.; Huang, J. S. High-Gain and Low-Driving-Voltage Photodetectors Based on Organolead Triodide Perovskites. *Adv. Mater.* **2015**, *27*, 1912–1918.

(19) Jeon, N. J.; Noh, J. H.; Yang, W. S.; Kim, Y. C.; Ryu, S. C.; Seo, J. W.; Seok, S. I. Compositional Engineering of Perovskite Materials for High-Performance Solar Cells. *Nature* **2015**, *517*, 476–480.

(20) Nie, W. Y.; Tsai, H. H.; Asadpour, R.; Blancon, J. C.; Neukirch, A. J.; Gupta, G.; Crochet, J. J.; Chhowalla, M.; Tretiak, S.; Alam, M. A.; Wang, H. L.; Mohite, A. D. High-Effciency Solution-Processed Perovskite Solar Cells with Millimeter-Scale Grains. *Science* **2015**, 347, 522–525.

(21) Mei, J. J.; Wang, F.; Wang, Y. P.; Tian, C. C.; Liu, H. Z.; Zhao, D. X. Energy Transfer Assisted Solvent Effects on CsPbBr₃ Quantum Dots. *J. Mater. Chem. C* 2017, *5*, 11076–11082.

(22) Kulbak, M.; Gupta, S.; Kedem, N.; Levine, I.; Bendikov, T.; Hodes, G.; Caben, D. Cesium Enhances Long-Trem Stability of Lead Bromide Perovskite-Based Solar Cells. *J. Phys. Chem. Lett.* **2016**, *7*, 167–172.

(23) Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon, C. H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V. Nanocrystals of Cesium Lead Halide Perovskites (CsPbX₃X = Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. *Nano Lett.* **2015**, *15*, 3692–3696.

(24) Dong, Y. H.; Gu, Y.; Zou, Y. S.; Song, J. Z.; Xu, L. M.; Li, J. H.; Xue, J.; Li, X. M.; Zeng, H. B. Improving All-Inorganic Perovskite Photodetectors by Preferred Orientation and Plasmonic Effect. *Small* **2016**, *12*, 5622–5632.

ACS Applied Materials & Interfaces

(25) Song, J. Z.; Xu, L. M.; Li, J. H.; Xue, J.; Dong, Y. H.; Li, X. M.; Zeng, H. B. Monolayer and Few-Layer All-Inorganic Perovskites as a New Family of Two-Dimensional Semiconductors for Printable Optoelectronic Devices. *Adv. Mater.* **2016**, *28*, 4861–4869.

(26) Zhou, L.; Yu, K.; Yang, F.; Cong, H.; Wang, N.; Zheng, J.; Zuo, Y. H.; Li, C. B.; Cheng, B. W.; Wang, Q. M. Insight into the Effect of Ligand-Exchange on Colloidal CsPbBr₃ Perovskite Quantum Dot/ Mesoporous-TiO2 Composite-Based Photodetectors: Much Faster Electron Injection. J. Mater. Chem. C **2017**, *5*, 6224–6233.

(27) Li, Y.; Shi, Z. F.; Li, S.; Lei, L. Z.; Ji, H. F.; Wu, D.; Xu, T. T.; Tian, Y. T.; Li, X. J. High-Performance Perovskite Photodetectors Based on Solution-Processed All-Inorganic CsPbBr₃ Thin Films. *J. Mater. Chem. C* **2017**, *5*, 8355–8360.

(28) Song, X. F.; Liu, X. H.; Yu, D. J.; Huo, C. X.; Ji, J. P.; Li, X. M.; Zhang, S. L.; Zou, Y. S.; Zhu, G. Y.; Wang, Y. J.; Wu, M. Z.; Xie, A.; Zeng, H. B. Boosting Two-Dimensional MoS₂/CsPbBr₃ Photodetectors via Enhanced Light Absorbance and Interfacial Carrier Separation. ACS Appl. Mater. Interfaces **2018**, 10 (3), 2801–2809.

(29) Shoaib, M.; Zhang, X. H.; Wang, X. X.; Zhou, H.; Xu, T.; Wang, X.; Hu, X. L.; Liu, H. W.; Fan, X. P.; Zheng, W. H.; Yang, T. F.; Yang, S. Z.; Zhang, Q. L.; Zhu, X. L.; Sun, L. T.; Pan, A. L. Directional Growth of Ultralong CsPbBr₃ Perovskite Nanowires for High-Performance Photodetecctors. *J. Am. Chem. Soc.* **2017**, *139*, 15592–15595.

(30) Liu, X. H.; Yu, D. J.; Cao, F.; Li, X. M.; Ji, J. P.; Chen, J.; Song, X. F.; Zeng, H. B. Low-Voltage Photodetectors with High Responsivity Based on Solution-Processed Micrometer-Scale All-Inorganic Perovskite Nanoplatelets. *Small* **2017**, *13*, 1700364.

(31) Yang, B.; Zhang, F. Y.; Chen, J. S.; Yang, S. Q.; Xia, X. S.; Pullerits, T.; Deng, W. Q.; Han, K. L. Ultrasensitive and Fast All-Inorganic Perovskite-Based Photodetector via Fast Carrier Diffusion. *Adv. Mater.* **2017**, *29*, 1703758.

(32) Cao, F.; Yu, D. J.; Li, X. M.; Zhu, Y.; Sun, Z. G.; Shen, Y. L.; Wu, Y.; Wei, Y.; Zeng, H. B. Highly Stable and Flexible Photodetector Arrays Based on Low Dimensional CsPbBr₃ Microcrystals and On-Paper Pencil-Drawn Electrodes. *J. Mater. Chem.* C **2017**, *5*, 7441–7445.

(33) Tong, G. Q.; Li, H.; Li, D. T.; Zhu, Z. F.; Xu, E. Z.; Li, G. P.; Yu, L. W.; Xu, J.; Jiang, Y. Dual-Phase CsPbBr₃–CsPb₂Br₅ Perovskite Thin Films via Vapor Deposition for High-Performance Rigid and Flexible Photodetectors. *Small* **2018**, *13*, 1702523.

(34) Liu, H.; Zhang, X. W.; Zhang, L. Q.; Yin, Z. G.; Wang, D. G.; Meng, J. H.; Jiang, Q.; Wang, Y.; You, J. B. A High-Performance Photodetector Based on an Inorganic Perovskite–ZnO Heterostructure. J. Mater. Chem. C 2017, 5, 6115–6122.

(35) Saidaminov, M. I.; Haque, M. A.; Almutlaq, J.; Sarmah, S.; Miao, X. H.; Begum, R.; Zhumekenov, A. A.; Dursun, I.; Cho, N.; Murali, B.; Mohammed, O. F.; Wu, T.; Bakr, O. M. Inorganic Lead Halide Perovskite Single Crystals: Phase-Selective Low-Temperature Growth, Carrier Transport Properties, and Self-Powered Photodetection. *Adv. Opt. Mater.* **2017**, *5*, 1600704.

(36) Song, J. Z.; Cui, Q. Z.; Li, J. H.; Xu, J. Y.; Wang, Y.; Xu, L. M.; Xue, J.; Dong, Y. H.; Tian, T.; Sun, H. D.; Zeng, H. B. Ultralarge All-Inorganic Perovskite Bulk Single Crystal for High-Performance Visible–Infrared Dual-Modal Photodetectors. *Adv. Opt. Mater.* **2017**, *5*, 1700157.

(37) Zhou, H.; Mei, J.; Xue, M. N.; Song, Z. H.; Wang, H. High-Stability, Self-Powered Perovskite Photodetector Based on a $CH_3NH_3PbI_3/GaN$ Heterojunction with C_{60} as an Electron Transport Layer. J. Phys. Chem. C **201**7, 121, 21541–21545.

(38) Ellmer, K. Past Achievements and Future Challenges in the Development of Optically Transparent Electrodes. *Nat. Photonics* **2012**, *6*, 809–817.

(39) Sebastian, M.; Peters, J. A.; Stoumpos, C. C.; Im, J.; Kostina, S. S.; Liu, Z.; Kanatzidis, M. G.; Freeman, A. J.; Wessels, B. W. Excitonic Emissions and Above-Band-Gap Luminescence in the Single-crystal Perovskite Semiconductors CsPbBr₃ and CsPbCl₃. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2015**, *92*, 235210.

(40) Saouma, F. O.; Stoumpos, C. C.; Kanatzidis, M. G.; Kim, Y. S.; Jang, J. I. Multiphoton Absorption Order of CsPbBr₃ As Determined by Wavelength-Dependent Nonlinear optical Spectroscopy. J. Phys. Chem. Lett. 2017, 8, 4912–4917.

(41) Zeng, J. P.; Li, X. M.; Wu, Y.; Yang, D. D.; Sun, Z. G.; Song, Z. H.; Wang, H.; Zeng, H. B. Space-Confined Growth of CsPbBr₃ Film Achieving Photodetectors with High Performance in All Figures of Merit. *Adv. Funct. Mater.* **2018**, *28*, 1804394.

(42) Cao, M.; Tian, J.; Cai, Z.; Peng, L.; Yang, L.; Wei, D. Perovskite Heterojunction Based on CH₃NH₃PbBr₃ Single Crystal for High-Sensitive Self-Powered Photodetector. *Appl. Phys. Lett.* **2016**, *109*, 233303.

(43) Lu, H.; Tian, W.; Cao, F.; Ma, Y.; Gu, B.; Li, L. A Self-Powered and Stable All-Perovskite Photodetector-Solar Cell Nanosystem. *Adv. Funct. Mater.* **2016**, *26*, 1296–1302.

(44) Dai, X. L.; Zhang, Z. X.; Jin, Y. Z.; Niu, Y.; Cao, H. J.; Liang, X. Y.; Chen, L. W.; Wang, J. P.; Peng, X. G. Solution-processed, High-Performance Light-Emitting Diodes Based on Quantum Dots. *Nature* **2014**, *515*, 96–99.

(45) Kamat, P. V.; Chauvet, J. P.; Fessenden, R. W. Photoelectrochemistry in Particulate Systems. 4. Photosensitization of a TiO₂ Semiconductor with a Chlorophyll Analogue. *J. Phys. Chem.* **1986**, *90*, 1389–1394.

(46) Jeong, K. S.; Tang, J.; Liu, H.; Kim, J.; Schaefer, A. W.; Kemp, K.; Levina, L.; Wang, X. H.; Hoogland, S.; Debnath, R.; Brzozowski, L.; Sargent, E. H.; Asbury, J. B. Enhanced Mobility-Lifetime Products in PbS Colloidal Quantum Dot Photovoltaics. *ACS Nano* **2012**, *6* (1), 89–99.

(47) Zhou, H.; Zeng, J. P.; Song, Z. N.; Grice, C. R.; Chen, C.; Song, Z. H.; Zhao, D. W.; Wang, H.; Yan, Y. F. Self-Powered All-Inorganic Perovskite Microcrystal Photodetectors with High Detectivity. *J. Phys. Chem. Lett.* **2018**, *9*, 2043–2048.

(48) Zhou, H.; Song, Z.; Grice, C. R.; Chen, C.; Yang, X.; Wang, H.; Yan, Y. Pressure-Assisted Annealing Strategy for High-Performance Self-Powered All-Inorganic Pervoskite Microcrystal Photodetectors. *J. Phys. Chem. Lett.* **2018**, *9*, 4714–4719.

(49) Li, Y.; Shi, Z. F.; Lei, L. Z.; Zhang, F.; Ma, Z. Z.; Wu, D.; Xu, T. G.; Tian, Y. T.; Zhang, Y. T.; Du, G. T.; Shan, C. X.; Li, X. J. Highly Stable Perovskite Photodetector Based on Vapor-Processed Micro-meter-Scale CsPbBr₃ Microplatelets. *Chem. Mater.* **2018**, *30*, 6744–6755.

(50) Stoumpos, C. C.; Maliakas, C. D.; Peters, J. A.; Liu, Z. F.; Sebastian, M.; Im, J.; Chasapis, T. C.; Wibowo, A. C.; Chung, D. Y.; Freeman, A. J.; Wessels, B. W.; Kanatzidis, M. G. Crystal Growth of the Perovskite Semiconductor CsPbBr₃A New Materials for High-Energy Radiation Detection. *Cryst. Growth Des.* **2013**, *13*, 2722–2727.