

High-Quality Cuboid $\text{CH}_3\text{NH}_3\text{PbI}_3$ Single Crystals for High Performance X-Ray and Photon Detectors

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Organic–inorganic halide hybrid perovskite materials are promising materials for X-ray and photon detection due to their superior optoelectronic properties. Single-crystal (SGC) perovskites have increasingly attracted attention due to their substantially low crystal defects, which contribute to improving the figures of merit of the devices. Cuboid $\text{CH}_3\text{NH}_3\text{PbI}_3$ SGC with the naturally favorable geometry for device fabrication is rarely reported in X-ray and photon detection application. The concept of seed dissolution-regrowth to improve crystal quality of cuboid $\text{CH}_3\text{NH}_3\text{PbI}_3$ SGC is proposed and a fundamental understanding of the nucleation and growth is provided thermodynamically. The X-ray detector fabricated from cuboid $\text{CH}_3\text{NH}_3\text{PbI}_3$ SGC demonstrates the firstly reported high sensitivity of $968.9 \mu\text{C}^{-1} \text{Gy}^{-1} \text{cm}^{-2}$ under -1 V bias. The results also show that the favorable crystal orientation and high quality of cuboid $\text{CH}_3\text{NH}_3\text{PbI}_3$ leads to better responsivity and faster response speed than the more common dodecahedral $\text{CH}_3\text{NH}_3\text{PbI}_3$ in photodetection. Consequently, the work paves a way to synthesize high-quality perovskite SGCs and benefits the application of MAPbI_3 SGCs with preferred crystal orientation and favorable crystal geometry for emerging device applications.

1. Introduction

Organic–inorganic halide hybrid perovskite materials in the formula of ABX_3 ($\text{A} = \text{Cs}^+$, CH_3NH_3^+ , $\text{HC}(\text{NH}_2)_2^+$; $\text{B} = \text{Pb}^{2+}$, Sn^{2+} ; $\text{X} = \text{Cl}^-$, Br^- , I^- , etc.), have attracted tremendous attention in optoelectronic applications because of their high absorption coefficient, long electron–hole diffusion length, high hole/electron mobility, direct and tunable bandgap, etc.^[1] Meanwhile, perovskites can be potential candidates as X-ray detectors widely applied in medical diagnosis and security purposes. X-ray detector with high sensitivity is crucial for lowering X-ray

dose limit, and thus minimizes radiation exposure. Comparing with polycrystalline films, single-crystal (SGC) perovskites offer superior advantages in X-ray detection because the density of grain boundaries and defects are substantially reduced, leading to high charge carrier mobility and lifetime product ($\mu\tau$) benefiting sensitivity enhancement.^[1i,2] $\text{CH}_3\text{NH}_3\text{PbBr}_3$ (MAPbBr_3) SGCs have been reported to exhibit superior X-ray attenuation capability and sensitivity in X-ray detection comparing with commercial $\alpha\text{-Se}$ X-ray detectors.^[1i,2b,c,3] In comparison with MAPbBr_3 , $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI_3) also has promising application in X-ray detection because of its higher $\mu\tau$ product and atomic number Z .^[4] Since X-ray absorption coefficient is proportional to Z^4 , the X-ray attenuation of MAPbI_3 is improved, as a result, the required crystal thickness for stopping 98% X-ray can be shortened by 50% (2 mm for MAPbBr_3 and 1 mm for MAPbI_3)^[1i] which largely reduce the

amount of Pb content to meet EU RoHS regulation limit.^[2e] Although thick $\text{CH}_3\text{NH}_3\text{PbI}_3$ films have been reported to be effective in X-ray detection,^[1h] the study of $\text{CH}_3\text{NH}_3\text{PbI}_3$ SGC X-ray detectors is rather limited because the natural geometry of MAPbI_3 SGCs is usually nonrectangular dodecahedrons (d- MAPbI_3 , with $\{100\}$ and $\{112\}$ facets exposed),^[2f,5] which is not as feasible as cuboid-shaped SGCs (such as $\text{CH}_3\text{NH}_3\text{PbBr}_3$ SGC) for device fabrications, especially for flat-panel arrays. Although ligand-mediated strategy was used to obtain cuboid MAPbI_3 (c- MAPbI_3 , with $\{110\}$ and $\{001\}$ facets exposed) SGCs, the residual ligands degrade the device performances.^[6] For the case without ligands, the shape of MAPbI_3 SGCs can be adjusted by tuning the proportion of halogen in the precursor to control the low-index-facet growth with high halogen density, but the optoelectronic properties and device applications are still missing probably due to the poor crystal quality.^[5] Consequently, while cuboid-shaped MAPbI_3 SGCs with natural favorable geometry for device fabrications are rarely studied, it is highly desirable to develop the strategy to obtain high-quality c- MAPbI_3 and investigate the effects of crystal facets orientation on physical properties and optoelectronic applications.

We herein report a new seed dissolution-regrowth (SDR) method to synthesize high-quality c- MAPbI_3 , which improves crystal quality by improving the structural matching between

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the seed and the subsequently deposited crystal to lower the required Gibbs free energy for nucleation. Our results show that c-MAPbI₃ synthesized with SDR had a long carrier lifetime of 497 ns, and its X-ray detector yielded a sensitivity of 968.9 $\mu\text{C}^{-1} \text{G}_\gamma^{-1} \text{cm}^{-2}$ under -1 V bias, higher than that of MAPbBr₃ SGCs counterpart. This is the first report of c-MAPbI₃ SGCs application in X-ray detection with the promising sensitivity. By comparing the X-ray and photon detection performances of c- and d-MAPbI₃ SGCs, we found that c-MAPbI₃ performs better than d-MAPbI₃ due to its conducive preferred crystal orientation for charge carrier diffusion and collection originated from the high quality of c-MAPbI₃ SGCs by SDR. Overall, our work paves the way to synthesize high-quality perovskite SGCs and demonstrate the advantages of MAPbI₃ SGCs with preferred crystal orientation for device applications.

2. Results and Discussion

Typically, c-MAPbI₃ SGCs were synthesized with inverse temperature crystallization (ITC), as depicted in the Supporting Information. In brief, the precursor with excess halogen (typically the molar ratio of PbI₂ and CH₃NH₃I (MAI) equals 1:2) is seeded and then gradually heated. Since the precursor solubility changes opposite to temperature, perovskite solute precipitates to expand the c-MAPbI₃ seed dimension in the heating process. The cubic shape results from the preferred

growth of halogen-crowded (100) facet over (110) facet in halogen-rich precursor. However, there are concerns about the poor quality of the crystals prepared by this method because of the defects or impurities on the seed surface, which serve as centers for heterogeneous nucleation. As shown by the scanning electron microscope (SEM) image in Figure 1a, a distinct gap ($\approx 10 \mu\text{m}$ in width) full of pin holes and grain boundaries exists between the seed and the subsequently crystallized part. The SEM image was taken from the region highlighted by the red rectangle in the inset, which shows the cuboid shape of the crystal but nonuniform surface. SEM image of c-MAPbI₃ at low magnification is shown in Figure S1a in the Supporting Information. After polishing off the crystal surface with 1800 mesh sandpaper to expose the inner crystal, we discovered that c-MAPbI₃ composed of a cluster of smaller cuboid crystals with loose structure, as shown in Figure 1b. The poor crystal quality of c-MAPbI₃ SGC will lead to poor optical and electrical properties, explaining its rare application in optoelectronic devices.

Differently, SDR process, as depicted in the Supporting Information, is proposed to improve the crystal quality of c-MAPbI₃, and the schematic diagram is shown in Figure S2 in the Supporting Information. The difference between SDR and ITC is that the precursor after seeding (Figure S2(I), Supporting Information) is kept at a relatively low temperature (110°C) for 15 min first (Figure S2(II), Supporting Information), and then gradually heated to target temperature (135°C) and incubated for seed regrowth (Figure S2(III), Supporting

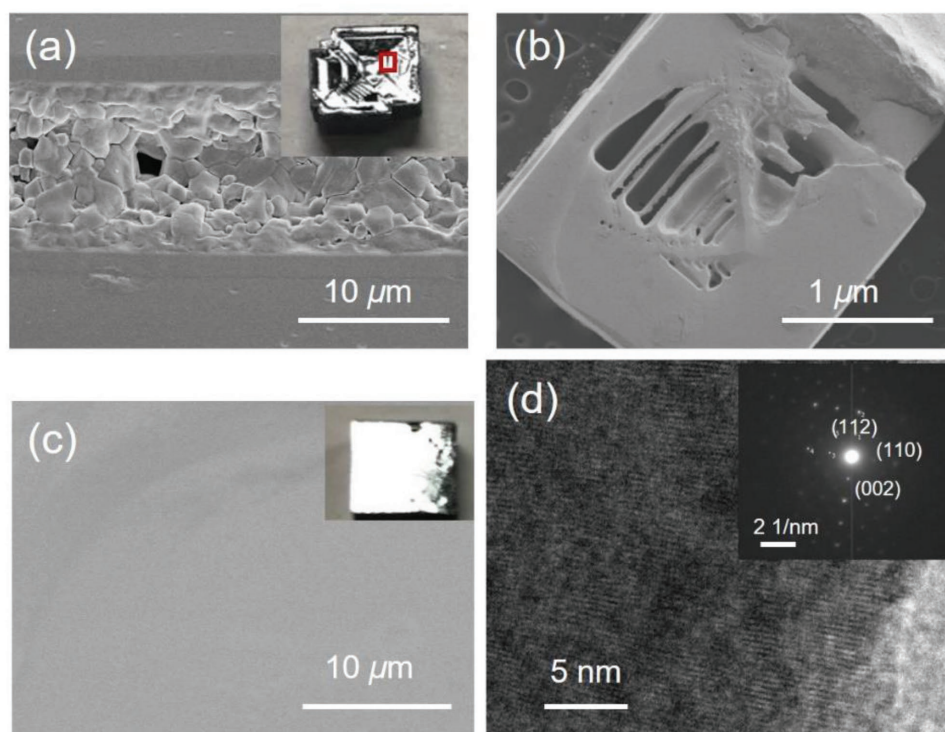


Figure 1. a) SEM image of c-MAPbI₃ SGC synthesized by typical ITC showing the gap full of grain boundaries and pin holes between the seed and the subsequently deposited part. The inset is the photograph of c-MAPbI₃ SGC by ITC, with the red rectangle indicating the site the SEM image taken. b) SEM image of the center part of c-MAPbI₃ SGC by ITC, which was exposed by polishing the c-MAPbI₃ SGC with sandpaper. c) SEM image of c-MAPbI₃ SGC synthesized by SDR showing the uniform morphology and dense structure without gaps observed between the seed and the subsequently deposited crystal. The inset is the photograph of c-MAPbI₃ by SDR. d) TEM image of c-MAPbI₃ SGC by SDR, and the lattice structure in the inset is the SAD pattern yielding the typical (110), (112), and (002) facets of tetragonal phase.

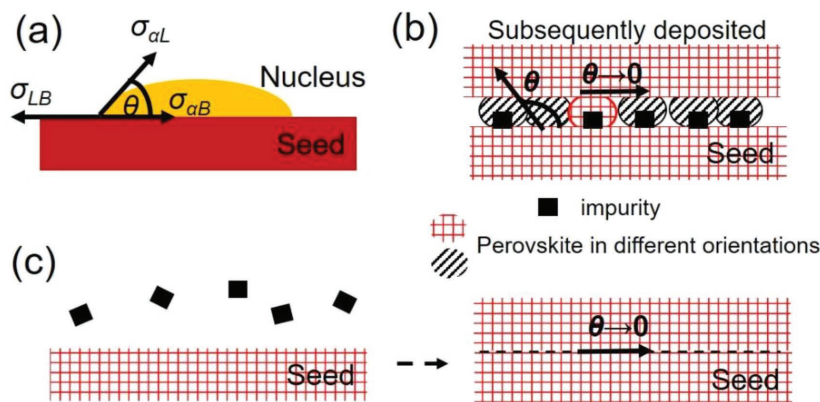


Figure 2. a) Schematic diagram illustrating the balance between the seed and the nucleus. b) Illustration for the gap defects formation between the seed and the subsequently deposited crystal with ITC synthesis. c) Illustration of the crystal quality improvement by enhancing the structural consistence between the seed and nucleus to avoid gap defects formation.

Information). As the SEM images shown in Figure 1c and that at low magnification in Figure S1b in the Supporting Information, c-MAPbI₃ SGC synthesized by SDR has uniform morphology and dense structure without gaps between the seed and the subsequently deposited crystal, confirming the specular reflection of c-MAPbI₃ SGC surface in the inset of Figure 1c. As shown in Figure 1d, the lattice structure in the transmission electron microscope (TEM) image of c-MAPbI₃ SGC, and the distinct diffraction lattice of selected-area diffraction (SAD) pattern in the inset suggests good crystallinity of the SGC. The SAD yields the typical (110), (112), and (002) facets, indicating the c-MAPbI₃ SGC belongs to tetragonal phase.

In order to understand the crystal quality improvement by SDR, we have studied the seeding and nucleation process thermodynamically. Generally, seeding will cause a great reduction of the required free energy (ΔG_K) for nucleation by providing ready-made surface of the seed. Considering the fact that one third of surface energy (ΔG_S) resulting from the formation of a new surface for homogeneous nucleation remains without being supplemented by unit volume free energy (ΔG_V), the residual surface energy (ΔG_S) needs to be compensated additionally.^[7] While for heterogeneous nucleation with seeding, ΔG_K relates to not only ΔG_S but also the wettability (depicted by contact angle, θ) between nucleus and the seed surface, expressed as

$$\Delta G_K = \frac{1}{3} \Delta G_S \left(\frac{2 - 3\cos\theta + \cos^3\theta}{4} \right) \quad (1)$$

Therefore, ΔG_K is reduced in comparison with homogeneous nucleation since the wettability-related factor in the parenthesis is normally in the range of 0–1.^[7] In equilibrium, the contact angle can be expressed by the following:

$$\cos\theta = \frac{\sigma_{LB} - \sigma_{\alpha B}}{\sigma_{\alpha L}} \quad (2)$$

where, σ_{LB} is the surface energy between liquid precursor and seed surface, $\sigma_{\alpha B}$ is that between nucleus and seed surface,

and $\sigma_{\alpha L}$ is that between nucleus and liquid precursor, as shown in Figure 2a. In order to minimize ΔG_K as much as possible, $\sigma_{\alpha B}$ should be close to 0, so that $\cos\theta$ approaches unity. Since $\sigma_{\alpha B}$ is determined by the structural similarity between nucleus and seed surface,^[7] the result suggests that the parameters on the atomic scale (e.g., atom size, spacing, and alignment, etc.) of nucleus and the seed should be as close as possible to minimize ΔG_K . For typical ITC, as shown by the schematic in Figure 2b, θ is rather large since the inevitably existed impurities on the seed surface increase the structural mismatch with the nucleus. As a result, ΔG_K still maintains at a high value, making it difficult to nucleate directly on seed surface. The impurities thus serve as nucleation centers and are wrapped by deposited perovskites.

Due to their structural similarity ($\theta \rightarrow 0$), cuboid perovskite deposits subsequently on wrapped perovskites with the same crystal orientation. Thus, c-MAPbI₃ SGCs grown by ITC with grain boundaries- and pinhole-rich gap sandwiched by the seed and the subsequently deposited perovskites, as shown in Figure 1a. In contrast for SDR, the seed dissolves and shrinks in the unsaturated precursor at the low temperature stage to remove the surface impurities (Figure 2c), which substantially decreases $\sigma_{\alpha B}$ ($\theta \rightarrow 0$) and improves structural consistency between the seed and the nucleus to lower ΔG_K for directly depositing perovskite on seed surface, avoiding gap defects formation between the seed and the subsequently deposited perovskites. We thus conclude that SDR has advantage in removing unfavorable defects in the final c-MAPbI₃ by improving structural consistency during crystal growth. SDR also benefits the attachment of c-MAPbI₃ on APTES((3-aminopropyl)triethoxysilane)-NH₃I functionalized Si substrates, which was reported to be effective in integrating MAPbBr₃ SGCs on substrates,^[2c] due to the improved structural matching between the seed facets and the new precipitates when $-\text{NH}_3\text{I}$ group reacted with PbI₂ in the solution, as shown in Figure S3 in the Supporting Information, which will make it feasible the integration of the cuboid crystals with thin-film substrates to form flat-panels.

To study the advantage of properties and device applications of c-MAPbI₃ SGCs, we synthesized d-MAPbI₃ SGCs for control, with detailed synthesis depicted in the Supporting Information. Powder X-ray diffraction (XRD) pattern in Figure 3a indicates the crystal structures of c- and d-MAPbI₃ belong to the tetragonal *14 cm* space group regardless of their different crystal orientations. SGC X-ray measurement of c-MAPbI₃ shows only (110) series of diffraction peaks, suggesting the upper facets of c-MAPbI₃ in the inset composed of (110) facet. XRD pattern of d-MAPbI₃ indicates the upper rhombic facet in the inset to be (100) series. The tetragonal (110) surface of MAPbI₃ is flat nonpolar facet consisting of alternate stacking of the neutral [MAI]⁰ and [PbI₂]⁰ planes, and the tetragonal (100) surface is constructed with stacking of the [MAPbI]²⁺ and [I₂]²⁻ layers.^[8] Therefore, c-MAPbI₃ and d-MAPbI₃ SGCs have totally different crystal orientations and unit cell stacking although they are

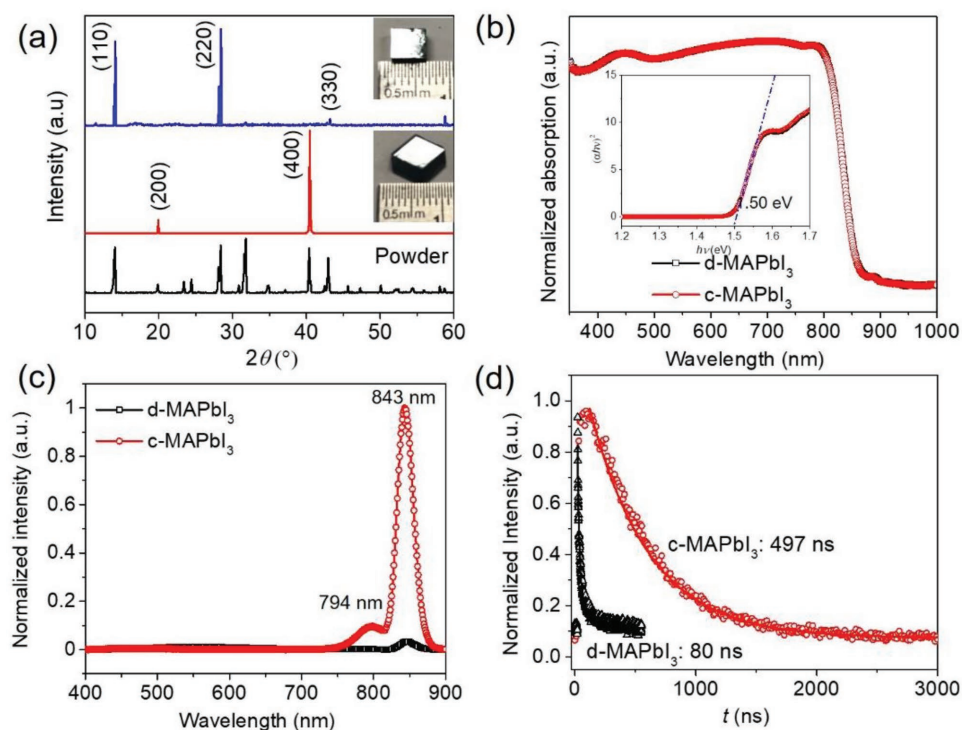


Figure 3. a) XRD pattern of c- (upper line) and d-MAPbI₃ SGC (middle line) and powder XRD pattern of MAPbI₃ (bottom line). The insets correspond to the photograph of c- (upper) and d-MAPbI₃ SGC (middle), respectively. b) UV-vis absorption spectra of c- and d-MAPbI₃ SGCs. The inset is the corresponding Tauc plots displaying the extrapolated optical bandgaps. c) Steady PL spectra of c- and d-MAPbI₃ SGCs. d) TRPL dynamics of c- and d-MAPbI₃ pumped with the same light wavelength and intensity.

both in tetragonal phase. As the ultraviolet–visible (UV–vis) absorption spectra shown in Figure 3b, c- and d-MAPbI₃ SGCs display an extended optical absorption cutoff to ≈ 850 nm, which are redshifted about 60 nm comparing with that of regular polycrystalline perovskite films (≈ 790 nm). The inset is the corresponding Tauc plots displaying the extrapolated optical bandgaps of 1.5 eV, smaller than polycrystalline bandgap of ≈ 1.55 eV, in accordance with reference that larger crystallites present smaller bandgap.^[3,9] The steady photoluminescence (PL) spectra shown in Figure 3c revealed two emission peaks of 794 and 843 nm, with the former representing the direct bandgap emission of perovskites and the latter the below-bandgap emission.^[2a,10] Meanwhile, both peaks of c-MAPbI₃ are much higher than that of d-MAPbI₃. Note that the shorter wavelength emission can be re-absorbed since the light absorption range of MAPbI₃ SGCs was broadened to ≈ 850 nm, which explained its weaker strength than that of the longer wavelength emission. The time-resolved photoluminescence (TRPL) dynamics of c- and d-MAPbI₃ are shown in Figure 3d, pumped with the same light wavelength (532 nm) and intensity. The PL decay curve of c-MAPbI₃ yielded a lifetime (τ) of 497 ns, well fitted by single-exponential decay model, while that for d-MAPbI₃ is only about 80 ns in average, comparative with the reference reported.^[5] The above results suggest the high crystal quality of c-MAPbI₃ SGCs by SDR and its good electrical properties in (110) orientation, which contributes to the long carrier lifetime because no mid-gap states observed in the electronic structures according to density functional theory calculation.^[8]

Hole-only devices with the structure of Au/cuboid MAPbI₃/Au were fabricated to derive the trap density N_t and hole mobility μ . As shown in Figure 4a, the linear Current–voltage (J – V) relation ($n = 1$) suggests an ohmic response at the low bias (< 2.9 V); a trap filling process was identified by the marked increase of the current injection ($n > 3$). N_t of c-MAPbI₃ SGC was calculated to be 1.14×10^9 cm⁻³, which is about an order of magnitude lower than the reported trap density of the d-MAPbI₃ SGCs ($\approx 1.4 \times 10^{10}$ cm⁻³)^[3] and six orders of magnitude lower than that of polycrystalline perovskite films,^[4] suggesting the advantageous crystal orientation and high crystal quality by SDR. μ was obtained by fitting the dark current of c-MAPbI₃ hole only devices according to Mott–Gurney law when operating in the trap-free space charge limit current (SCLC) regime ($n = 2$), and a value of ≈ 293 cm² V⁻¹ s⁻¹, which is larger than that of d-MAPbI₃ SGCs (≈ 164 cm² V⁻¹ s⁻¹)^[4] and the optimized MAPbBr₃ SGCs (≈ 217 cm² V⁻¹ s⁻¹)^[11,3] was derived. Using μ and τ , the hole diffusion length (L_D) was derived to be 31 μ m for MAPbI₃ SGCs, which is higher than that previously reported for d-MAPbI₃ SGCs (10 μ m) and that of MAPbBr₃ SGCs (4.3 μ m).^[3] Detailed calculations of N_t , μ , and L_D are depicted in the Supporting Information.

The large mobility μ and long charge carrier lifetime τ yield a desirable high $\mu\tau$ production for c-MAPbI₃, which offers the better average carrier drift distance per unit electric field, and thus enhances charge collection efficiency at a given electric field. Experimentally, we employed the modified Hecht equation to fit the photoconductivity to derive the $\mu\tau$ product, a

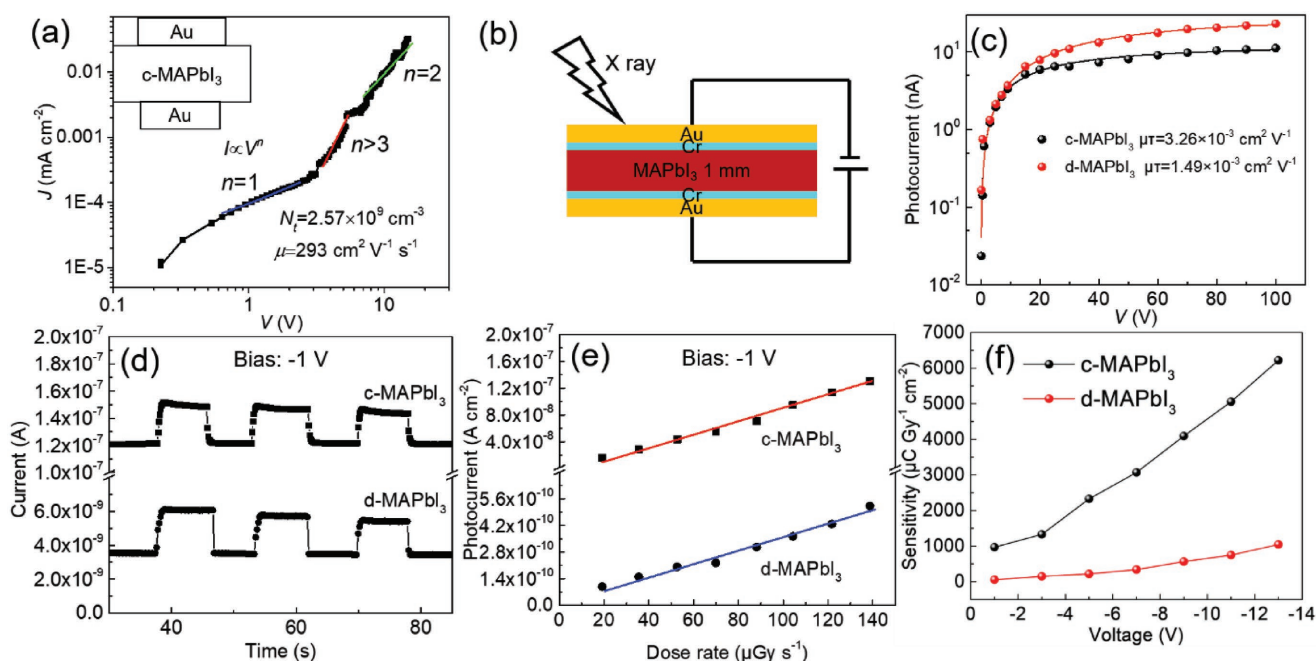


Figure 4. a) J - V curve of hole-only devices with the structure of Au/c-MAPbI₃/Au to derive the trap density and hole mobility. b) Schematic diagram of X-ray detector with 1 mm thick c- or d-MAPbI₃ SGCs sandwiched between chromium (Cr)/gold (Au) electrodes. c) Bias-dependent photoconductivity of c-MAPbI₃ and d-MAPbI₃. Hecht equation was used to fit the photoconductivity data. d) Current response of c- and d-MAPbI₃ SGC-based X-ray detectors under -1 V bias. e) Photocurrent-dose rate relation of c- and d-MAPbI₃ SGCs X-ray detectors under -1 V bias for the derivation of sensitivity. f) Sensitivity of c-MAPbI₃ and d-MAPbI₃ under different biases.

method widely applied in semiconductor radiation detector.^[11] As shown in Figure 4c, the d-MAPbI₃ SGC had a $\mu\tau$ product of 1.49×10^{-3} cm² V⁻¹ and c-MAPbI₃ SGC exhibited a higher value of 3.26×10^{-3} cm² V⁻¹, which was consistent with the trend of carrier mobility.

In addition, the heavier atomic number Z of iodine (53) for MAPbI₃ than that of bromine (35) for MAPbBr₃ can benefit the absorption coefficient α for stopping X-ray, which is sensitive to Z according to the relation $\alpha \propto Z^4/E^3$,^[11] where E is the X-ray photon energy. We therefore applied c-MAPbI₃ SGCs in X-ray detectors, in which 1 mm thick c-MAPbI₃ SGCs (only half of the reported MAPbBr₃ SGCs^[11]) sandwiched between two chromium (Cr)/gold (Au) electrodes with a mask area of 4 mm², as shown in Figure 4b. The x-ray tube, with a tungsten anode and a 2 mm Al plate as the filter, was conducted under an accelerating voltage of 50 kV and the peak intensity located at 30 keV. The X-ray spectrum shown in Figure S4 in the Supporting Information. d-MAPbI₃ SGC-based X-ray detector with the same device structure serves as a control to gain insight on the effect of crystal orientation on device performance. As shown in Figure 4d, c-MAPbI₃-based X-ray detector has a good photocurrent response of $\approx 1.5 \times 10^{-7}$ A under -1 V bias, while that for d-MAPbI₃ X-ray detector is about two orders of magnitude lower. The sensitivity of X-ray detectors is evaluated with dose rate in the range of 19.13–138.7 μ Gy s⁻¹ under -1 V bias, as shown in Figure 4e. The sensitivity of c-MAPbI₃-based X-ray detector is about 968.9 μ C Gy⁻¹ cm⁻² with linear fitting (the solid line) and the sensitivity of d-MAPbI₃-based X-ray detector in this work is only ≈ 3.4 μ C Gy⁻¹ cm⁻². The sensitivity of c-MAPbI₃-based X-ray detector was higher than that of

MAPbBr₃-based device (322 μ C Gy⁻¹ cm⁻²) under same bias.^[2c] It should be noted that the MAPbBr₃-based device was illuminated by an Ag target X-ray tube with highest energy up to 50 keV and the peak energy at 22 keV. As we used a X-ray tube with highest energy up to 50 keV and peak energy at 30 keV, we think the test condition were basically the same. c-MAPbI₃ X-ray detector obtained a higher sensitivity under higher photon energy X-ray illuminated, which shown that the outstanding performance of c-MAPbI₃ in X-ray detection. Upon enhancing the bias to -13 V, the sensitivity of c-MAPbI₃ linearly increased to 6218 μ C Gy⁻¹ cm⁻², as shown in Figure 4f. As for d-MAPbI₃, the sensitivity can only reach 1045 μ C Gy⁻¹ cm⁻² under same bias. The results confirm the high $\mu\tau$ production originating from the favorable crystal orientation and good crystal quality and of c-MAPbI₃ by SDR.

Furthermore, we found the same superior advantages of c-MAPbI₃ SGCs over d-MAPbI₃ SGCs in photodetectors. The schematic diagram of the photodetector is shown in Figure 5a, with the dimension of active channel between two adjacent electrodes 4 mm $\times$ 100 μ m. J - V curves of the photodetectors were measured in dark and under illumination using 550 nm LED with light intensities ranging from 0.05 to 60 mW cm⁻², as shown in Figure S5a,b in the Supporting Information. For c-MAPbI₃ SGC photodetector, the current rises from 10^{-9} A in dark to more than 10^{-4} A under 60 mW cm⁻² illumination, while that for d-MAPbI₃ SGC photodetector ranges from 10^{-7} A to 10^{-5} A. The much lower dark current of c-MAPbI₃ SGC photodetector than d-MAPbI₃ SGC photodetector results from the good crystal quality by SDR. Responsivity (R , the photocurrent generated per unit of incident light power), external

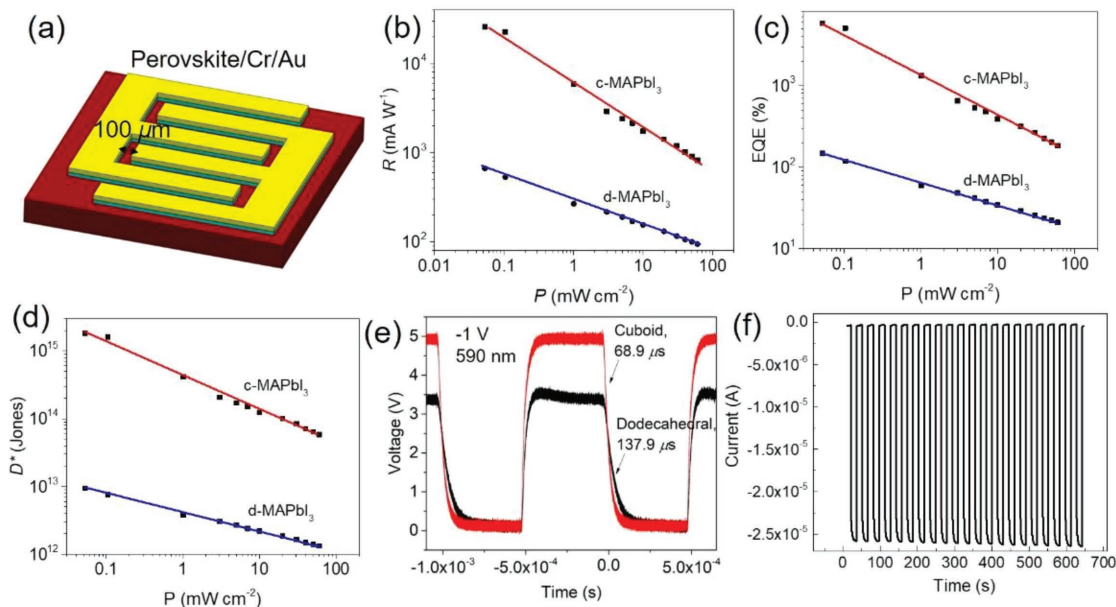


Figure 5. Schematic diagram of MAPbI₃ SGC photodetector, with the dimension of active channel between two adjacent electrodes as 100 μm. b–d) are responsivity (R), EQE, and detectivity (D^*), respectively, determined from the J – V results under -1 V bias, which were measured in dark and under illumination using 550 nm LED with light intensities ranging from 0.05 to 60 mW cm⁻², as shown in Figure S5 in the Supporting Information. e) Response time of c- and d-MAPbI₃ SGC photodetectors under -1 V bias measured with 590 nm light. f) Light response of c-MAPbI₃ SGC photodetectors by continuously switching the light for 20 times every 15 s.

quantum efficiency (EQE), and detectivity (D^*) (shot noise limited) were determined from the J – V results under -1 V bias, as shown in Figure 5b–d, respectively. The calculation details are depicted in the Supporting Information. R , EQE, and D^* all decrease linearly with increasing light intensity because more charge recombination is expected under higher light intensity.^[2b] R , EQE, and D^* of c-MAPbI₃-based photodetector are at least an order of magnitude higher than those for d-MAPbI₃-based one under all the light intensity. Highest R , EQE, and D^* for c-MAPbI₃ SGC photodetector are achieved with values of about 2.6×10^4 mA W⁻¹, 5700%, and 1.8×10^{15} Jones, respectively, while those for d-MAPbI₃ SGC photodetector are 660 mA W⁻¹, 140%, and 9.4×10^{12} Jones, respectively. The results suggest that (110) orientation of c-MAPbI₃ is much more sensitive in light detection than (100) of d-MAPbI₃. The rather high EQE (>100%) also suggests the photodetectors belong to photoconductor type, in which one type of charge carrier is able to circulate through an external circuit many times before it recombines with its opposite carrier.^[12] The response time of c- and d-MAPbI₃ SGC photodetectors under -1 V bias is shown in Figure 5e. Response time is the period when the photocurrent increases from 90% to 10% of the saturated value. A fast response of 68.9 μs was obtained for c-MAPbI₃ SGC photodetector, which confirms the high crystal quality with SDR synthesis since the response speed of a photodetector is strongly related to charge transport and collection. Meanwhile, the response time for d-MAPbI₃ SGC photodetector is much longer (137.7 μs), almost double that for c-MAPbI₃ SGC photodetector, and the voltage response is also lower than that of c-MAPbI₃ SGC photodetector. It should be noted that the physical mechanism of photodetector decay time is different from that of PL lifetime. PL lifetime is measured under no external

bias, and is influenced by the radiative and nonradiative recombination rate. On the contrary, the detector decay time is measured under bias voltage, and is determined by the carrier transit time ($\tau = d^2/\mu U$, where d is the carrier transit length and U is bias)^[13] and trap lifetime.

In addition, as PL lifetime is influenced by nonradiative recombination, the longer PL lifetime of perovskite is an indicator of lower concentration of defect states.^[14] Less defect can avoid the carrier scattering effect, and thus result in higher carrier mobility, which has been observed in many previous works.^[15] In our case, we also found the carrier mobility of c-MAPbI₃ (PL lifetime: 497 ns) is higher than d-MAPbI₃ (80 ns). Moreover, we could qualitatively compare the detector response time by calculating the carrier transit time. From the SCLC results, we know that the μ of d-MAPbI₃ is 121 cm² V⁻¹ s⁻¹ (see Figure S6, Supporting Information) and c-MAPbI₃ is 293 cm² V⁻¹ s⁻¹. The transit time ratio between c-MAPbI₃ and d-MAPbI₃ is 1:2.4, which agrees well with the photodetector decay time. These results suggest the poorer photodetection ability of (100) orientation than (110) for MAPbI₃ perovskite. In addition, we monitored the response time of c- and d-MAPbI₃ SGC photodetectors under very low bias (-0.1 V), as shown in Figure S7 in the Supporting Information. We found that c-MAPbI₃ SGC photodetector had fast response speed while d-MAPbI₃ SGC photodetector did not respond effectively. This implies that c-MAPbI₃ SGC photodetector has a rather wide bias range of photodetection response. When we switch the incident light for 20 times every 15 s, the measured response data follow closely to the switching, indicating reliable light detection, as shown in Figure 5f. Consequently, our c-MAPbI₃ photodetector offer much better responsivity and faster response speed than that of d-MAPbI₃ counterpart.

3. Conclusion

In summary, we demonstrate high-quality c-MAPbI₃ SGCs by proposing SDR method, which improves crystal quality by improving the structural matching between the seed and the subsequently deposited crystal. Interestingly, very low trap density, long carrier life time, and very high carrier mobility have been achieved for c-MAPbI₃ SGC synthesized by SDR, ensuring the promising applications in X-ray detector and planar photodetector. X-ray detectors with SDR c-MAPbI₃ SGCs showed a high sensitivity of 968.9 $\mu\text{C}^{-1} \text{Gy}^{-1} \text{cm}^{-2}$ under -1 V bias, which is the first report of c-MAPbI₃ SGC application for X-ray detection. Based on the high crystal quality and favorable crystal orientation, c-MAPbI₃ photodetector showed better responsivity and faster response speed than d-MAPbI₃ counterpart. Our work provides a way to synthesize high-quality SGCs and show the advantage of MAPbI₃ SGCs with preferred crystal orientation for emerging device applications, which will provide a guidance for further improving the performance of perovskite devices through crystal orientation adjustment.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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