Supplementary files for

Optimizing Optoelectronic Performances by Controlling Halide Compositions for $MAPb(Cl_xI_{1-x})_3$ Single Crystals

Zhiwen Xu [a], Huadong Li [a, #], Hongyang Zhao [a, *], Qiuming Fu [a], Hong Tao [a], Shenggao Wang [a], Zhibin Ma [a, b], Jianxu Ding [c, *], Yongfu Ma [d], Yibo Han [d, *]

[a] *Hubei Key Laboratory of Plasma Chemistry and Advanced Materials, Wuhan Institute of Technology, No. 206 Guanggu 1st Road, Wuhan 430205, China*

[b] *Huanggang Normal University, Huanggang 436100, China*

[c] *College of Materials Science and Engineering, Shandong University of Science and Technology, Qingdao 266590, China*

[d] *Wuhan National High Magnetic Field Center and School of Physics, Huazhong University of Science and Technology, Wuhan 430074, China*

Corresponding Author

E-mail: zhaohy@wit.edu.cn (Hongyang Zhao)

E-mail: dingjianxu@sdust.edu.cn (Jianxu Ding)

γ-butyrolactone (γ-GBL) (≥99%), PbI_2 (≥98%), $PbCl_2$ (≥99%), N,N-dimethylformamide (DMF) (≥99.5%) and Dimethyl sulfoxide (DMSO) (≥99%) were purchased from Sinopharm Chemical Reagent Co. LTD. CH_3NH_3I (≥99.5%), CH_3NH_3Cl (≥99.5%) was purchased from Xi'an Polymer Light Technology Corp.

The Cl concentrations in the starting materials are $MAPb(Cl_xI_{1-x})_3$ (x=0, 0.01, 0.04, 0.05, 0.06, 0.20, 0.99, 0.1). But it is difficult to achieve the doping of Cl above the composition of 0.20 (in raw solutions) into $MAPbI_3$ (x>0.20). In fact, the Cl

concentrations in the as-grown crystals are much less than in the starting solutions. We used EDS to measure the Cl concentrations in as-grown crystals. Compared to the initial concentration of Cl in the solution with the values of 0, 0.01, 0.04, 0.05, 0.06, 0.20, the doping concentrations of Cl in the as-grown crystals were 0, 0.0055, 0.0089, 0.0105, 0.0122 and 0.1173, respectively. The crystals could not be obtained with large amount doping of Cl. Sometimes the solution is not stable and the mixed crystals or meta-crystals are obtained. Table 1 shows the molar ratio of Cl in starting solution and as-grown crystals.

Table S1 The initial molar ratio of Cl in solution and the actual molar ratio of Cl in as-grown crystals

Initial ratio	0	0.01	0.04	0.05	0.06	0.20	0.99	1.0
Actual ratio	0	0.0055	0.0089	0.0105	0.0122	0.1173	0.989	1

The lattice parameters were calculated through the refinement using the software of MAUD. The detailed data were shown in the following Table 2. The lattice parameters of a and c decrease from $CH_3NH_3PbI_3$ to $CH_3NH_3PbCl_3$. The lattice strain between $CH_3NH_3PbI_3$ to $CH_3NH_3PbCl_3$ is shown in Figure S1.

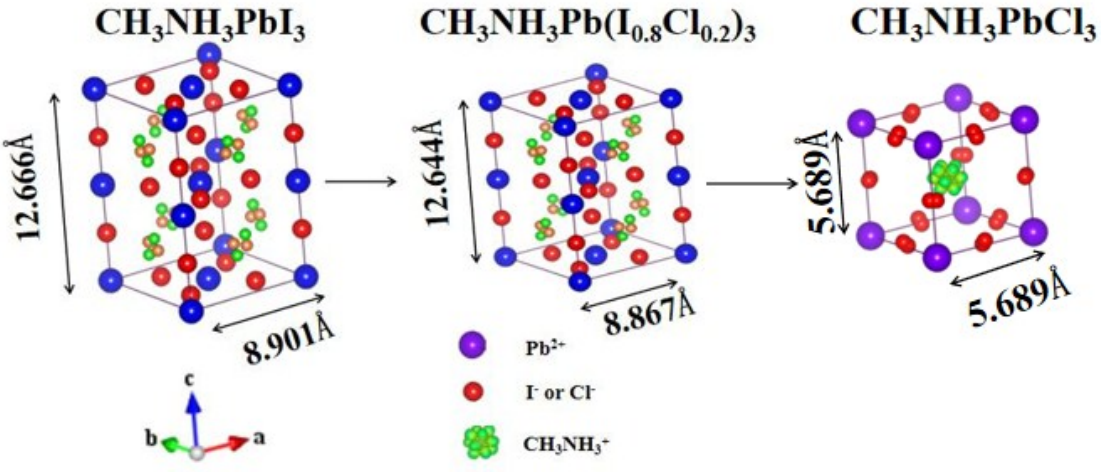

Figure S1. The lattice strain between $CH_3NH_3PbI_3$ and $CH_3NH_3PbCl_3$.

Table S2 The lattice parameters were calculated through the refinement using the software of MAUD.

lattice parameters	a	c
x=0	8.901	12.666
x=0.01	8.882	12.662
x=0.04	8.88	12.655
x=0.05	8.879	12.654
x=0.06	8.872	12.653
x=0.20	8.867	12.644

Optoelectronic Performances

The parameters of the five $MAPb(Cl_xI_{1-x})_3$ photodetectors were shown in Table S3. We determined the values of rise time (τ_{rise} - required time for current rising to 90%) and decay time (τ_{decay} - required time for current falling to 10%).

The photoresponsivity(R) was calculated as follows,

$$R=\frac{I_{light}-I_{dark}}{P_{light}*S}$$

where I_{light} is the photocurrent(A), I_{dark} is the dark current(A), S is the area of contact(cm^2) and P_{light} is the incident light power(W).

specific detectivity(D) was calculated as follows,

$$D=\frac{R}{\sqrt{2e*J_{dark}}}$$

Where R is the spectral responsivity(mA/W), J_{dark} is the dark current(A/cm^2) and e is the electronic charge(C). Jones=$cm*Hz^{\frac{1}{2}}/W$.

External quantum efficiency(EQE) was calculated as follows,

$$EQE = \frac{R * hc}{e * \lambda}$$

where R is the spectral responsivity(mA/W), h represents the Planck's constant, c stands for the velocity of light(m/s), e is the electronic charge(C) and λ is the wavelength of incident light(nm).

Table S3 The parameters of the six $MAPb(Cl_xI_{1-x})_3$ photodetectors.

x	x=0	x=0.01	x=0.04	x=0.05	x=0.06	x=0.20
Rise time(s)	0.65	1.47	1.14	0.66	0.51	0.65
Decay time(s)	0.15	0.65	0.17	0.16	0.16	0.17
R(mA/W)	0.025	0.125	0.825	2.575	5.725	9.525
EQE(%)	0.0057	0.0283	0.1865	0.5821	1.2942	2.1531
D($\times 10^{10}$ jones)	0.0215	0.1077	0.7108	2.2185	4.9324	8.2062

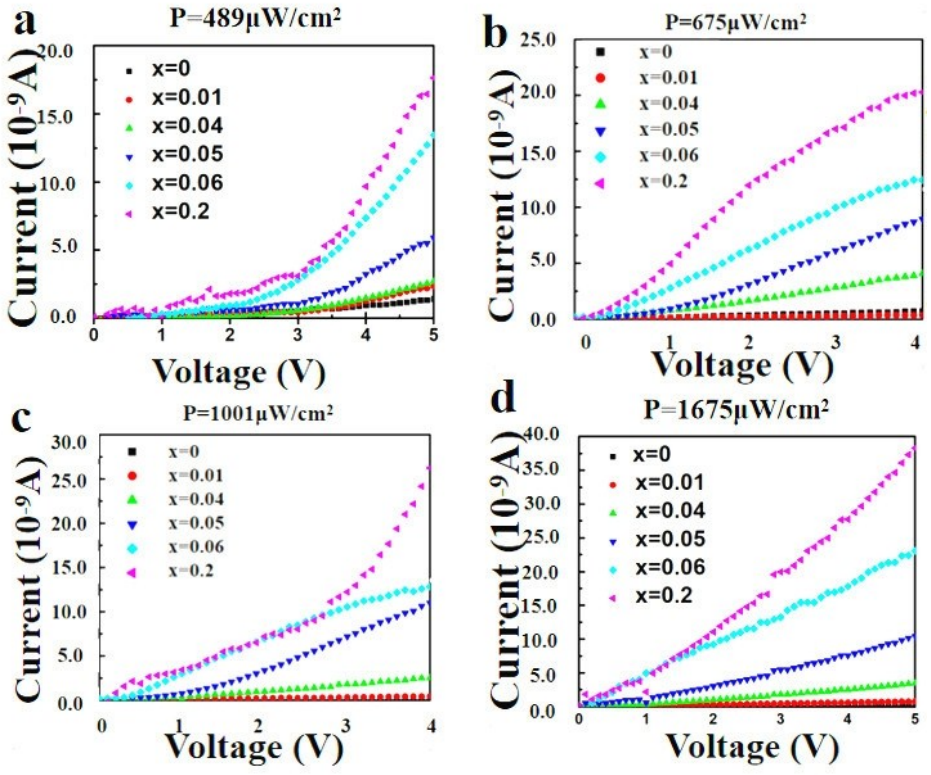

Fig. S2. I−V characteristic of six $MAPb(Cl_xI_{1-x})_3$ (x=0, 0.01, 0.04, 0.05, 0.06, 0.20) photodetectors

under the illumination of (a) 489 μW/cm^2, (b) 675μW/cm^2, (c) 1001μW/cm^2 and (d) 1609 μW/cm^2.

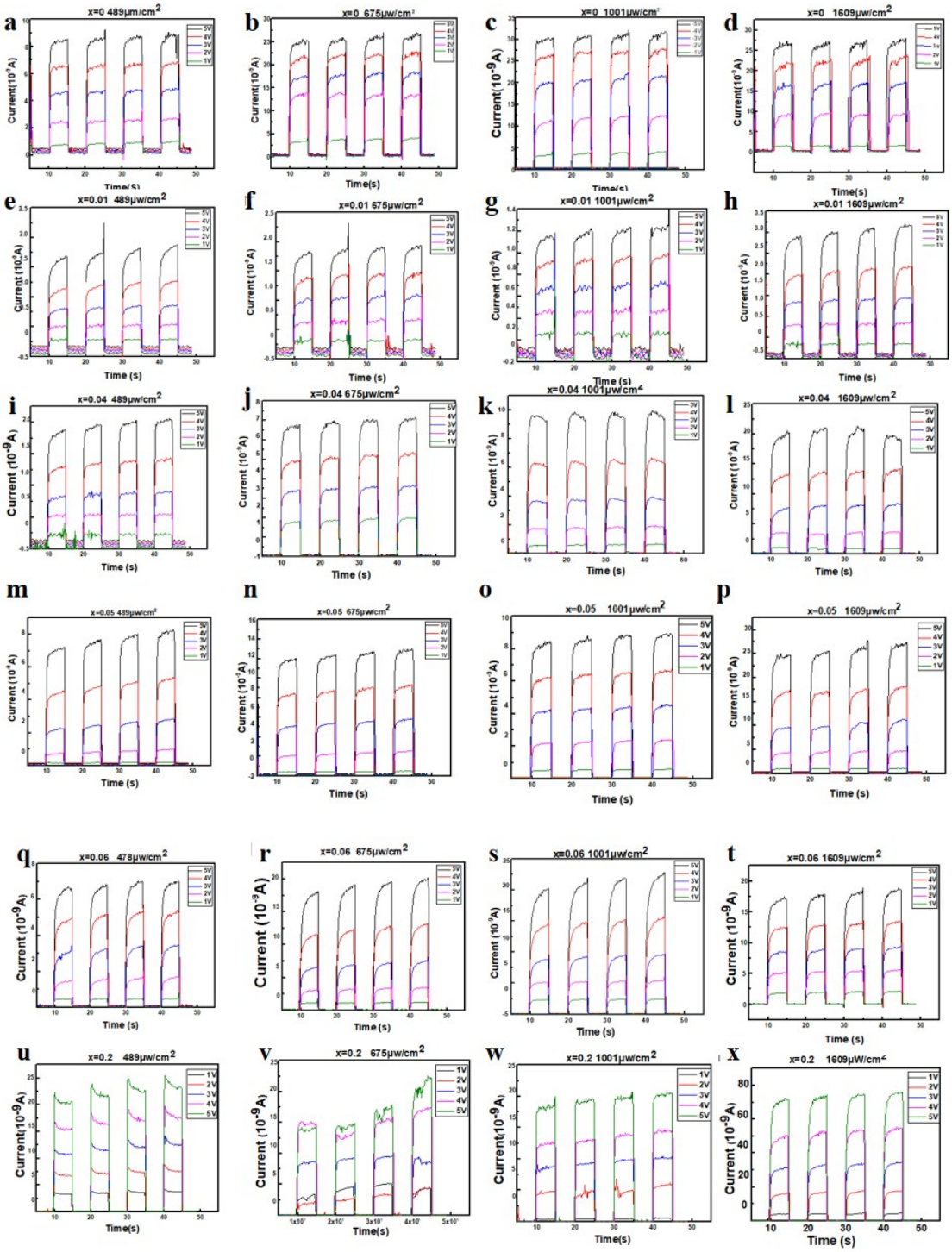

Fig. S3. The photocurrent response of the device with the illumination (360 nm, 489 μW/cm^2 675μW/cm^2, 1001μW/cm^2 and 1609 μW/cm^2) switched on and off at different bias voltages for four cycles.

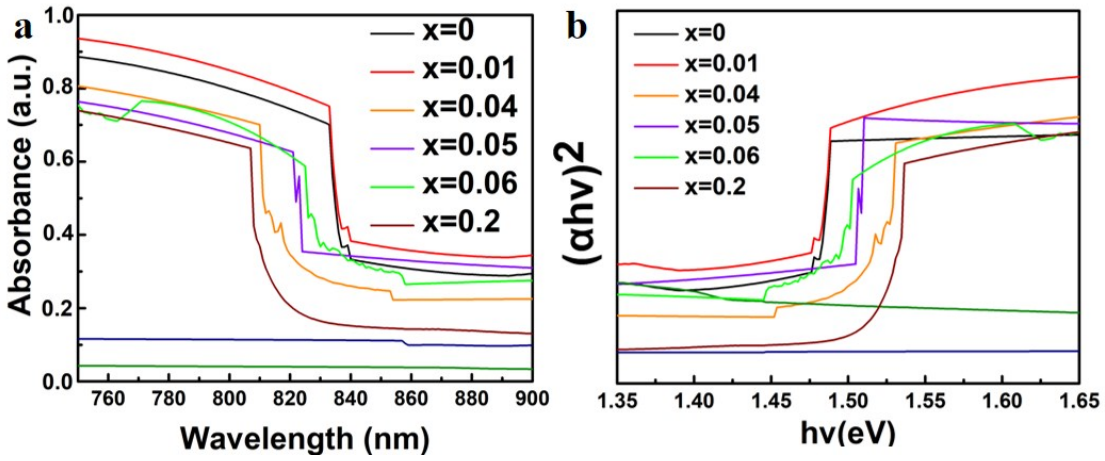

Fig. S4. The enlarged spectrums to distinguish the parts for crystals of x<0.2.

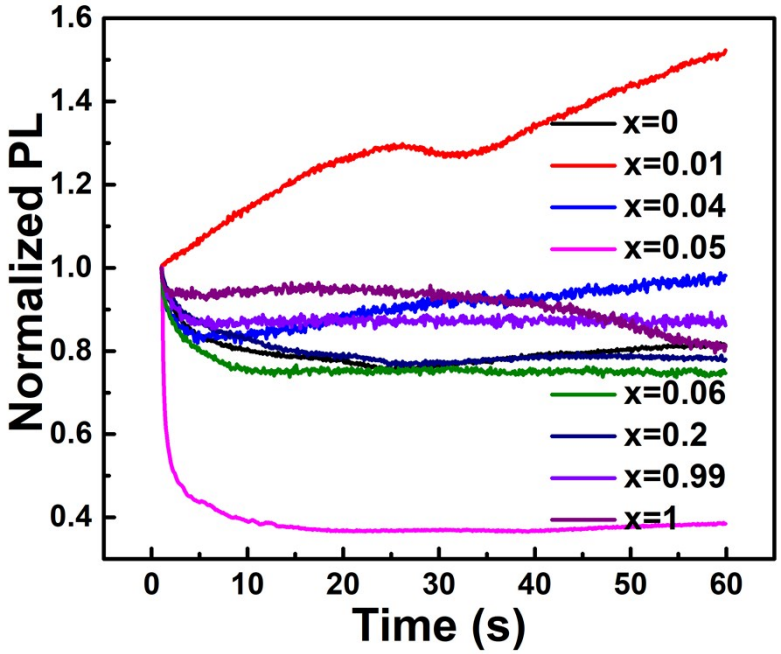

Fig. S5. Time-resolved PL profiles of $MAPb(I_{1-x}Cl_x)_3$ under λ_{exc} = 350 nm CW excitation (I_{exc} = 5 mW cm^{-2}) over the course of 60 seconds.

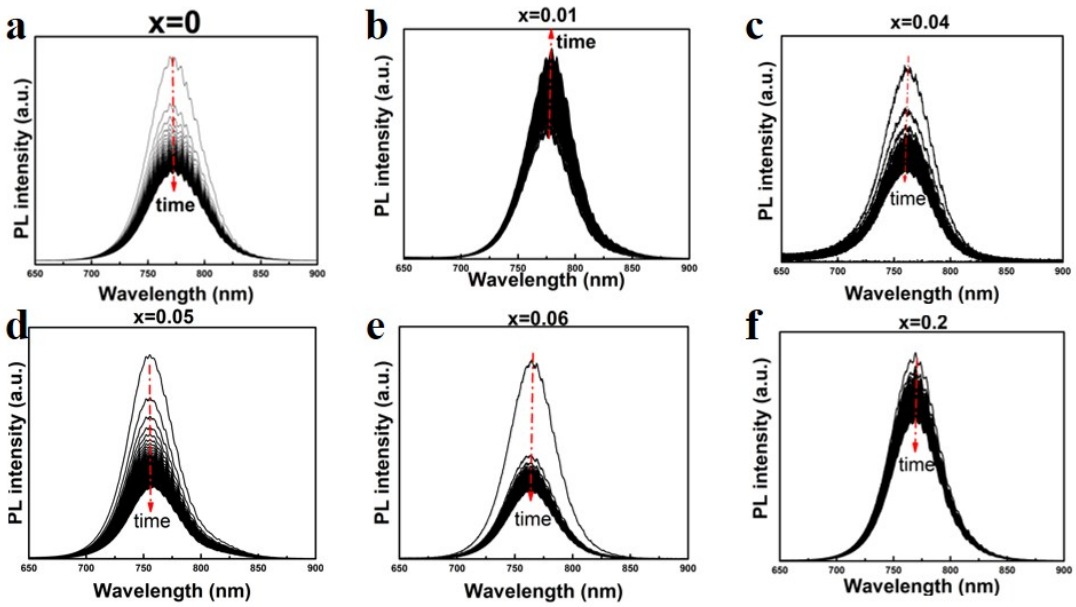

Fig. S6. Time-dependent PL spectra.