ELECTRONIC SUPPLEMENTARY INFORMATION

Density of photoinduced free carriers in perovskite thin films via purely optical detection

Yu Li,[a] Wei Wang,[a] Xiangyuan Wang,[c] Shufeng Wang,*[a,b] Yantao Shi[c] and Qihuang Gong[a,b]

[a] *State Key Laboratory for Artificial Microstructure and Mesoscopic Physics, School of Physics, Peking University, Beijing 100871, China*

[b] *Collaborative Innovation Center of Extreme Optics, Shanxi University, Taiyuan, Shanxi 030006, China*

[c] *State Key Laboratory of Fine Chemicals, School of Chemistry, Dalian University of Technology, Dalian, Liaoning 116024, China*

*Corresponding author. wangsf@pku.edu.cn

Experimental Methods

$CH_3NH_3PbI_3$ films. They were deposited on cleaned glass slides with a two-step sequential method in a nitrogen atmosphere. First, 70 µL of a pre-heated (70 ℃) solution of PbI_2 in DMF (N,N-Dimethylformamide, 1 M) was spin-coated on the substrate at 5000 r.p.m. for 10 s and sequentially annealed at 70 ℃. After cooling to room temperature, the samples were dipped in 2-propanol for 10 s before being transferred and dipped into a CH_3NH_3I 2-propanol (10 mg/ml) solution for 2 min. Then the films are rinsed with 2-propanol and dried by spin-coating at 3000 r.p.m. for 30 s. Finally annealing was performed at 70 ℃ to obtain the perovskite thin films.

$CH_3NH_3PbI_{3-x}Cl_x$ films. For the deposition of Cl-doped films, a precursor solution of 174.9 mg CH3NH3I and 102.2 mg $PbCl_2$ in 0.5 ml DMF was initially prepared. Films were deposited in a nitrogen atmosphere. First, 70 µL of a pre-heated (70 ℃) precursor solution was spin-coated on the clean substrate at 2000 r.p.m. for 30 s. Then annealing was performed at 90 ℃ for 1 h and sequentially another 25 min at 100 ℃ obtain the perovskite thin films.

Characterizations. The elemental composition in the films was measured by X-ray photoelectron spectroscopy (XPS) with an AXIS Ultra instrument (Kratos UK). The crystallinity of the films was characterized by X-ray diffraction (XRD) on a Rigaku D/Max-2400 diffractometer. All samples were prepared on clean glass substrates.

Spectroscopic method. The light source is a mode-lock Ti:sapphire femtosecond laser system (Legend, Coherent) pumped two-stage optical parametric amplifier (OperA Solo, Coherent). It generates pump pulse of 517 nm at repetition rate of 1 KHz, with pulse width ~200 fs and energy up to 100 µJ per pulse. The temporal-spectral fluorescence were recorded with a streak camera

system (Hamamatsu C10910) centered at 780 nm. Short time windows of 5 ns were applied to resolve PL_0. The continuous light is 532 nm from a diode laser. All samples were hold in a cryostat under nitrogen atmosphere with pulsed and continuous irradiation from two perpendicular windows.
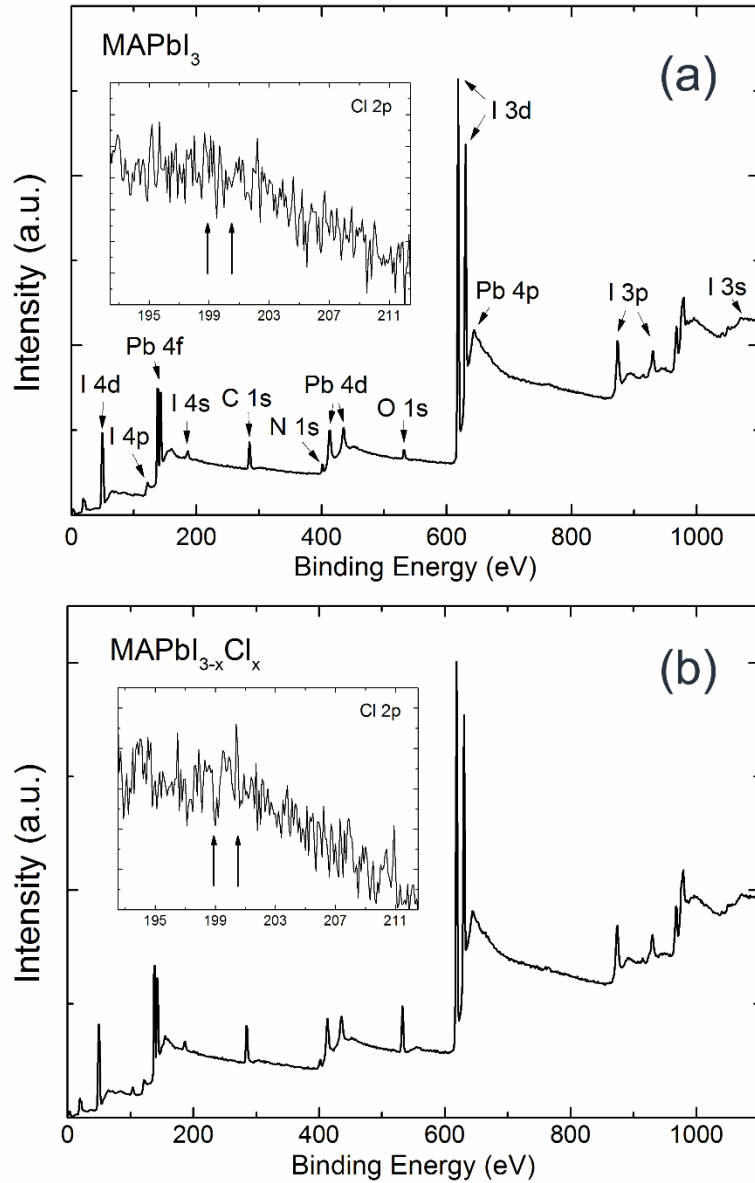
FIG. S1. The XPS survey spectra of the top surface of (a) pure $CH_3NH_3PbI_3$ and (b) $CH_3NH_3PbI_3$ films with chlorine introduction. Insets are the corresponding Cl2p core level XPS spectra, characteristic peak binding energy of $Cl2p_{3/2}$ and $Cl2p_{1/2}$ (198.9 eV and 200.5 eV) highlighted by the arrows.
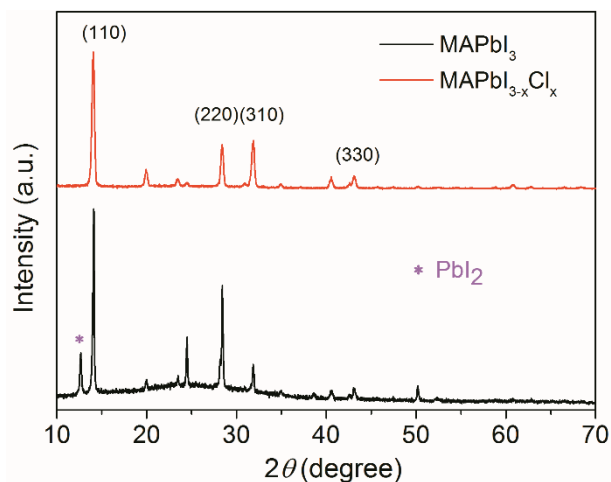
FIG. S2. The XRD patterns of $CH_3NH_3PbI_3$ films with and without chlorine introduction. The conversion of PbI_2 into final perovskite product is completed with Cl introduction, consistent with previous reports (*Adv. Funct. Mater.* **24,** 7102-7108 (2014); *J. Phys. Chem. C* **119,** 15868-15873 (2015)), proving that the introduction of Cl favors the crystallization of perovskite, possibly by slowing down the formation process. Meanwhile, both samples present the same characteristic perovskite peaks, showing that the final products are $CH_3NH_3PbI_3$ type, with little amount of Cl element remaining, in agreement with XPS results in Fig. S1. Interestingly, comparing with the pure iodine sample, the crystallinity of the film with chlorine introduction does not get improved, with characteristic peaks modestly broadening, suggesting that there is very small amount of Cl present and having an impact on crystal lattices. In all, we can conclude that very little Cl could exist and might affect material properties, such as crystal structure, electronic behaviors and thus optical properties.
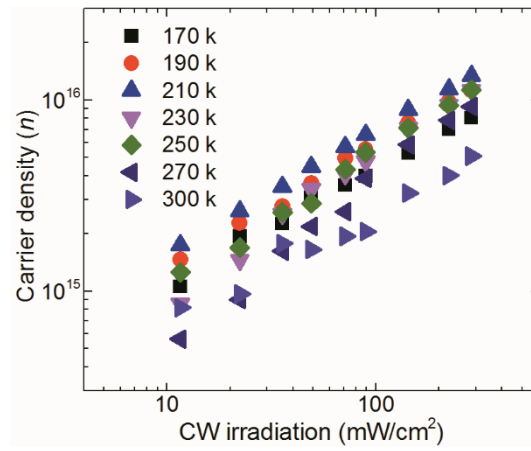
FIG. S3. The temperature dependence measurement of charge carrier density of Cl-free $CH_3NH_3PbI_3$ films towards the increment of CW laser intensity.
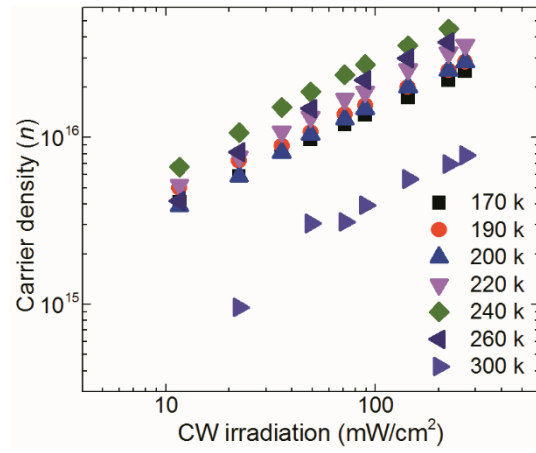
FIG. S4. The temperature dependence measurement of charge carrier density of Cl-doped $CH_3NH_3PbI_3$ films towards the increment of CW laser intensity.

.

Table S1. Accumulated spatial carrier density detected by pulsed light carrier detection method.

$I_{c,pump}$ (mW/cm²)	Carrier injection (10^{21}·cm⁻³·s⁻¹)	$I_{p,pump}$ (nJ/cm²)	n_p (10^{15}·cm⁻³)	F_p	F_{p+c}	n_c (10^{15}·cm⁻³)	$\overline{n_c}$ (10^{15}·cm⁻³)	$\overline{1/k}$ (µs)
0	0	14	1.5	1.1			0	
		25	2.6	4.0				
18	1.9	14	1.5		2.2	0.62	0.60	0.32
		25	2.6		6.0	0.58		
49	5.3	14	1.5		4.0	1.36	1.40	0.26
		25	2.6		9.6	1.43		

$I_{c,pump}$ and Carrier injection are the intensity of continuous light at 532 nm and corresponding excitation density at unit time. $I_{p,pump}$ and n_p are the pulsed light energy and corresponding excitation injection per pulse. F_p is the fluorescent intensity with pulsed light only. F_{p+c} is the PL_0 when combine continuous and pulsed light. n_c is the calculated spatial charge density under continuous illumination, with expression $n_c = n_p \left(\sqrt{I_{c+p}} - \sqrt{I_p}\right)/\sqrt{I_p}$. $\overline{n_c}$ is the average value of n_c, while $\overline{1/k}$ is the carrier lifetime calculated by $G = kn_c$, where G represents the continuous carrier injection.

.