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Photon-generated Carriers Excited Superoxide Species Inducing Long-term Photoluminescence Enhancement of $MAPbI_3$ Perovskite Single Crystals

Xiyuan Feng,[1]† Huimin Su,[2]† Yinghui Wu,[1,3] Han Wu,[1] Jian Xie,[1] Xinke Liu,[4] Jing Fan,[2] Junfeng Dai,[2,]* Zhubing He[1,]*

[1]*Department of Materials Science and Engineering, Shenzhen Key Laboratory of Full Spectral Solar Electricity Generation (FSSEG), Southern University of Science and Technology, No. 1088, Xueyuan Rd.,518055, Shenzhen, Guangdong, P.R. China*

[2]*Department of Physics, Southern University of Science and Technology, No. 1088, Xueyuan Rd.,518055, Shenzhen, Guangdong, P.R. China*

[3]*Department of Physics, Chongqing University, No. 55, University City South Rd. 401331, Chongqing, P. R. China*

[4]*College of Materials Science and Engineering, Guangdong Research Center for Interfacial Engineering of Functional Materials, Shenzhen University, No. 3688, Nanhai Ave, 518060, Shenzhen, P.R. China*

†*X.Y. and H.M. contribute equally to this work.*

**Corresponding authors: hezb@sustc.edu.cn; dajjf@sustc.edu.cn*

1. Materials

Methylamine (33 wt. % solution in absolute ethanol) and Hydriodic acid (57wt.% solution in H_2O) were purchased from Acros Co. Ltd. and lead acetate trihydrate (99%) was purchased from Tianjin Kemiou Chemical Reagent Co. Ltd. Oxygen (99.999%) and nitrogen (99.999%) gases were provided by Air Products and Chemicals Inc.. All chemicals were used as received except specially mentioned.

2. Synthesis and Characterizations of $MAPbI_3$ single crystal

$MAPbI_3$ single crystals were synthesized in solution by temperature-lowering (TL) method. A 250ml round-bottom flask charged with 29.3g lead acetate trihydrate was put into ice-water bath, followed by slowly adding 100ml hydriodic acid and keeping stirring at a proper rate throughout process of the experiment. Then, 8 ml of methylamine solution was added slowly in dropwise into the

flask until the solution turned yellow. Successively, the flask was taken out from the ice-water bath and heat at 80℃ for 4 hours with continuous stirring. After that, the yellow mixture solution was put in a little bottle (25ml) and stored in a 100℃ oven 20 hours. With the decrease of the oven temperature from 100 to 70 ℃ at a rate of 0.5℃ per hour, the black and shiny crystal of $MAPbI_3$ was successfully grown at the bottom after a few days. Powder X-Ray diffraction pattern of $MAPbI_3$ single crystals was obtained with Rigaku smart Lab at room temperature with 45% in humidity.

3. Photoluminescence (PL) measurements

PL measurements were performed by exciting the samples with a Coherent Sapphire SF 532 nm-150 CW laser. The laser power was adjusted by a series of filters. PL was collected into a Hriba 320 spectrometer with a 300 lines/mm grating and recorded with an InGaAs charged-coupled device (CCD) (Andor iDus)In addition,778 nm irradiation light was purchased also from Coherent Inc.. 808 nm and 980 nm CW irradiation lasers are semiconductor one provided by SFOLT and Oclaro Inc., respectively.

In vacuum, a chamber with quartz window for optical measurements was evacuated for at least 15 mins to reach below 1×10^{-3} Pa via a molecular pump (1.5 kHz). From the vacuum state to oxygen or nitrogen gas environments, the chamber was directly infiltrated with testing gases after at least 30 mins of vacuuming. From nitrogen to oxygen atmosphere, evacuation of the chamber for at least 30 mins was also needed before putting in oxygen gas. The purity of oxygen and nitrogen gas involved in this experiment is over 99.999%.

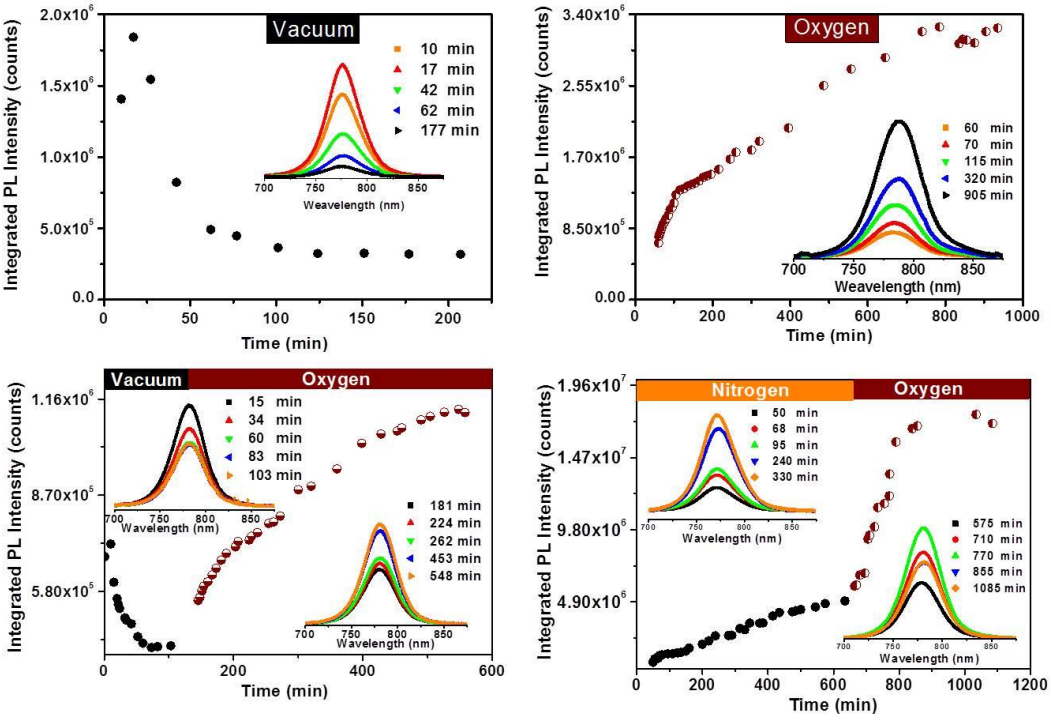

Figure S1. Integrated PL intensity as a function of light soaking time excited by a 532 nm laser with power of 300 μW under various environments. Each PL intensity was measured under 532nm laser excitation with power of 15 μW at the blind interval of soaking light. (a) In vacuum. (b) In oxygen atmosphere. (c) and (d) transitions from vacuum to oxygen and nitrogen to oxygen, respectively.

4. PL lifetime measurement

PL lifetime curves were collected by a photon counting system with system resolution of 0.25ns (PicoHarp 300, PicoQuant Inc). The PL was excited by 150 fs laser pulses with a repetition rate of 80 MHz and 2.33 eV photon energy (Chameleon vision laser system from Coherent Inc). Due to limitation of the repetition frequency of excitation pulse laser, the maximum span of PL is around 12.5ns. Non-zero PL intensity before time zero shown in **Fig. 2b** and **Fig. S2** indicates that PL lifetime is longer than 12.5ns. In addition, because the signal from laser is negligible around 0.5 ns as indicated by dot line of **Fig. S2**, the data for exponential fit are started after 0.5ns. By considering non-zero PL intensity before time zero and fitting PL data by mono- (bi-) exponential function, we deduced one (two) time constants and listed it in **Table S1**.

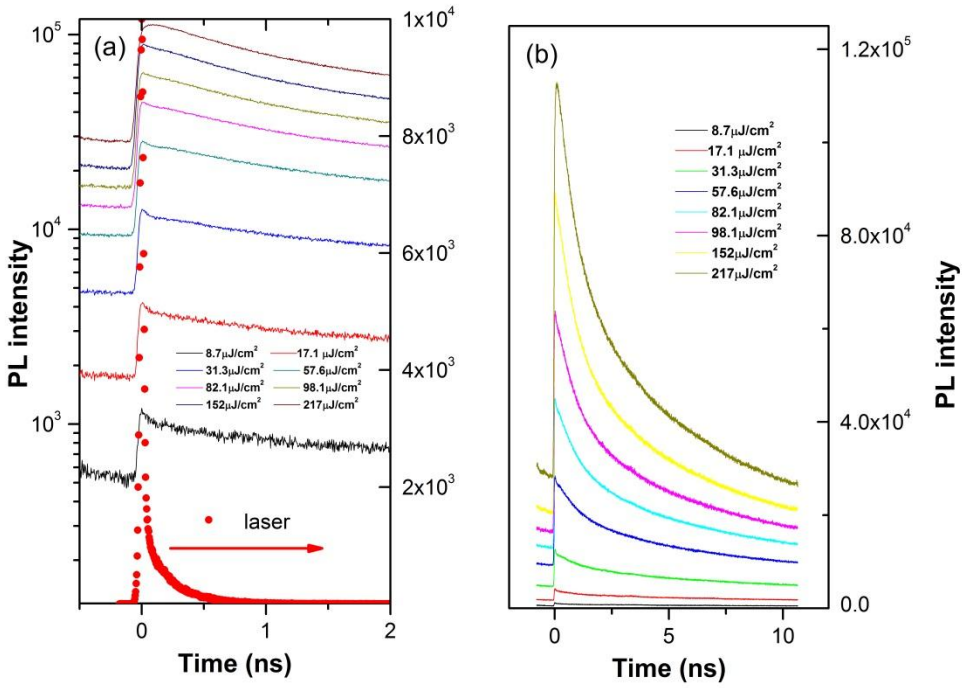

Figure S2. (a) PL transients under various excitation fluences ranging from 8.7 $\mu J/cm^2$ to 217 $\mu J/cm^2$ within 2 ns timescale. The dots data represent the laser lifetime. (b) The PL transients under various excitation fluences ranging from 8.7 $\mu J/cm^2$ to 217 $\mu J/cm^2$ under linear scale.

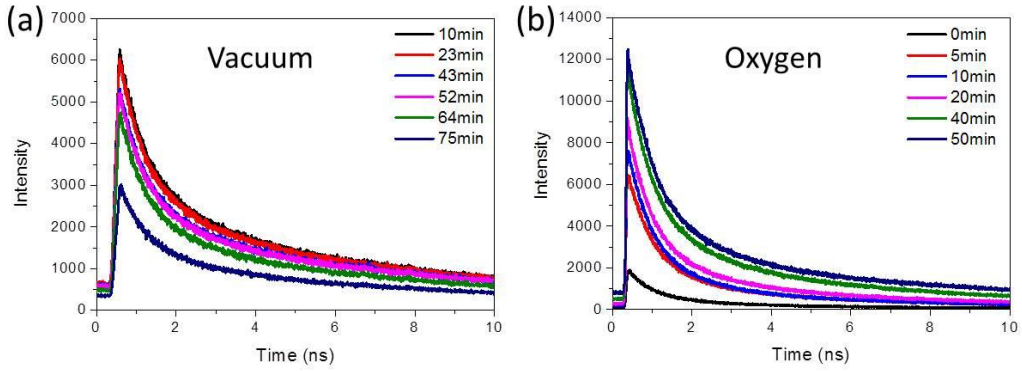

Figure S3. PL transients after different time of 300 μW 532 nm laser light soaking in vacuum (a) and oxygen atmosphere (b).

Table S1. The PL lifetime fitted by mono- (bi-) exponential function

Excitation fluences (μJ/ cm²)	**8.7**	**17.1**	**31.3**	**57.6**	**82.1**	**98.1**	**152**	**217**

Lifetime constant (t_1/ns)	**22**	**29**	**24**	**20**	**18**	**16**	**14**	**13**
Lifetime constant (t_2/ns)	**/**	**2.8**	**2**	**1.7**	**1.5**	**1.5**	**1.4**	**1.4**

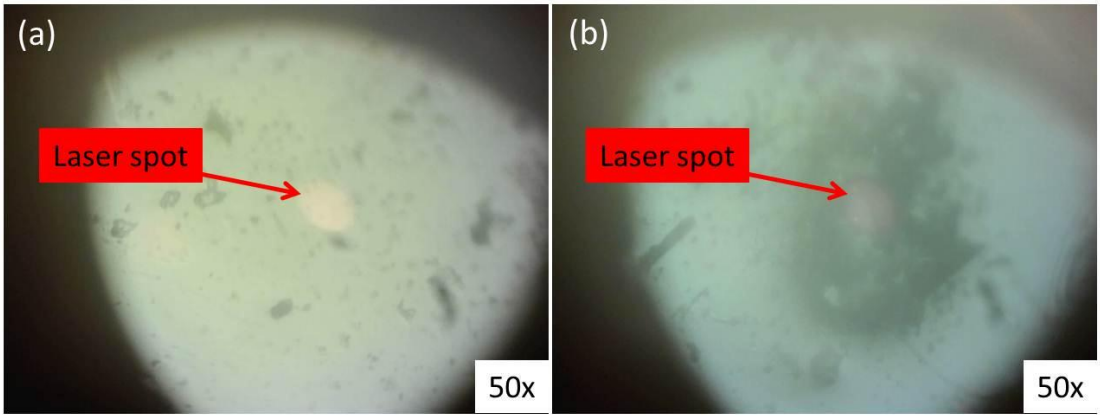

Figure S4. 50X microscopy image of the $MAPbI_3$ single crystal's surface morphology of the pristine (a) and after over 1 hour irradiation of 532 nm laser with 1mW in power (b). The latter shows the surface damage clearly.

5. Confocal microscopy system

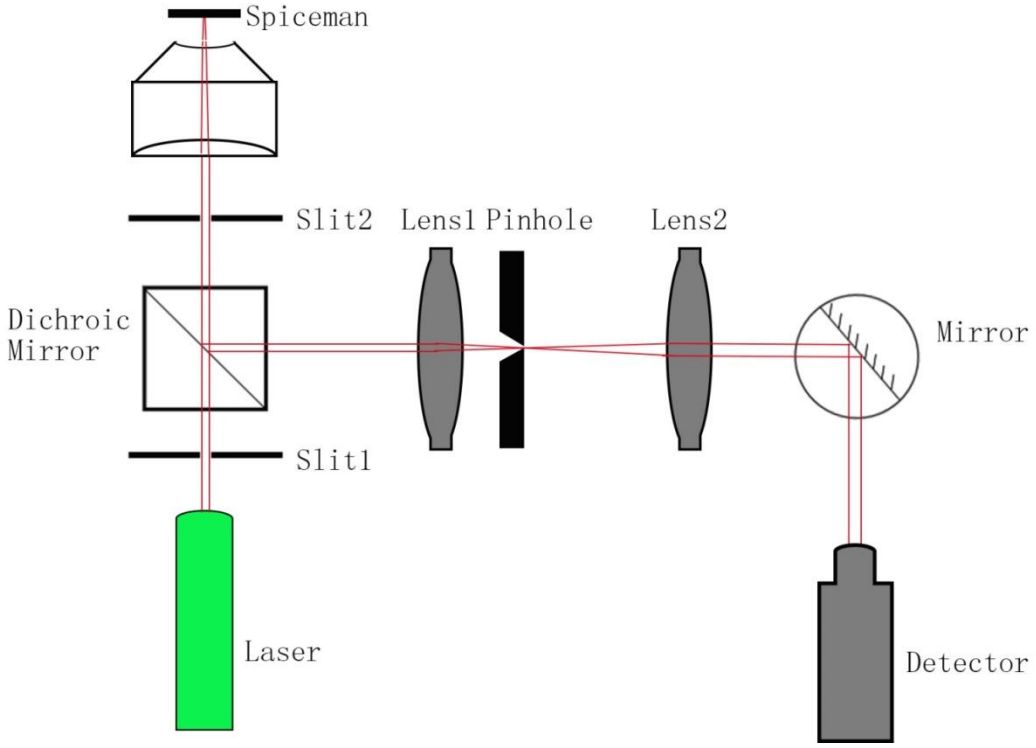

Figure S5. Schematic set-up of a home-built confocal microscopy system for PL measurements in depth profile.