Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Optical Characterizations of Surface States in Hybrid Lead-Halide Perovskites

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1. Sample Characterizations

Time-resolved PL spectra were measured by an Edinburgh FLS920 spectroscopy system. The excitation source is a 405/635 nm laser with picosecond pulse with power density of 5nJ/cm^2.

X-ray diffraction (XRD) was carried out on a PANalytical X-ray diffractometer (Model EMPYREAN) with a monochromatic Cu Ka1 radiation. The lattice parameters were precisely determined using Si powders as the internal standard reference material.

X-ray photoelectron spectroscopy (XPS) measurement was carried out by integrate ultrahigh vacuum system equipped with multifunction surface analysis system (ESCALAB 250Xi) with monochromatized Al Kα(1486.6eV) X-ray radiation source. The work function and Fermi level were calibrated. The samples were good indium contacted with the equipment. Ag 3d (368.2) was used to calibrate the XPS data.

Scanning electron microscopy (SEM) characterization was performed with a Hitachi S4800 operating at an acceleration voltage of 5 kV.

2. Near-band-edge optical properties of $MAPbI_3$.

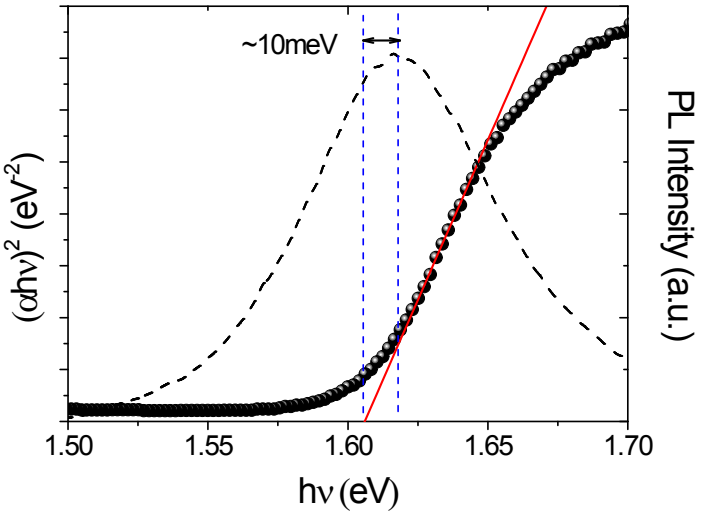


Fig.S1 Absorption and PL spectra of Sample A. The bandgap is determined to be 1.606eV. The PL peak shows an obvious Stokes shift (~10 meV) located at 1.616eV. The results agree well with previous reports.[1, 2]

2. Determination of VBM for Sample A and B.

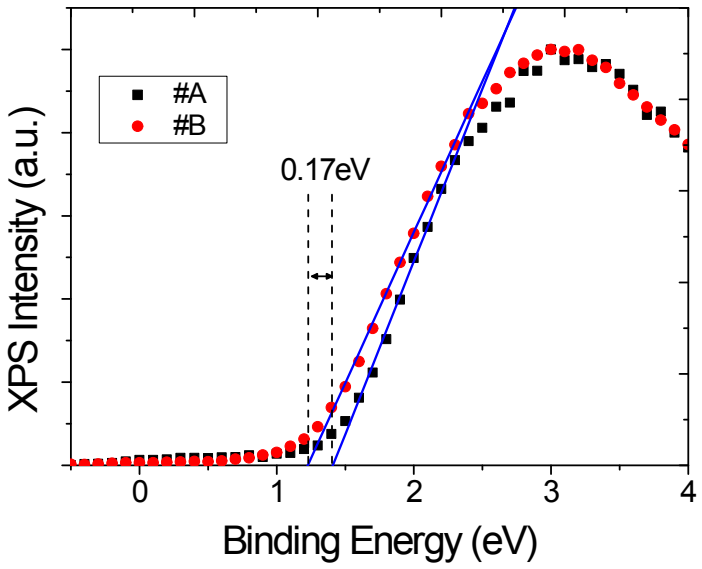
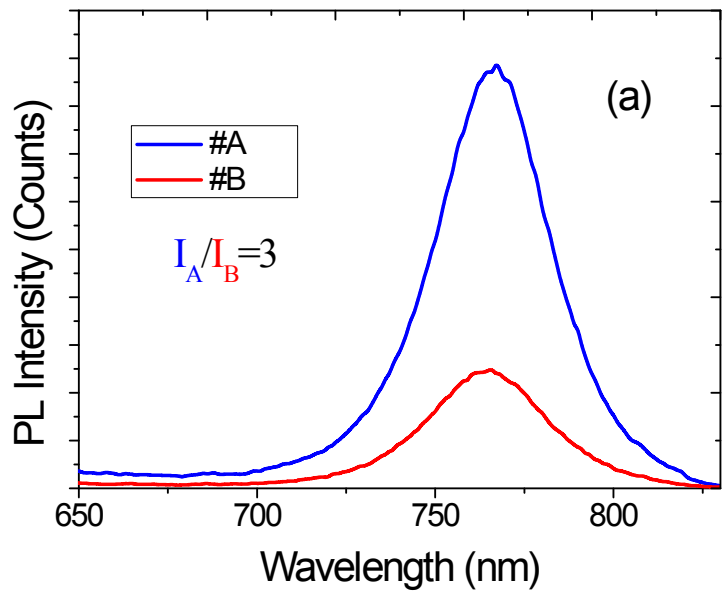
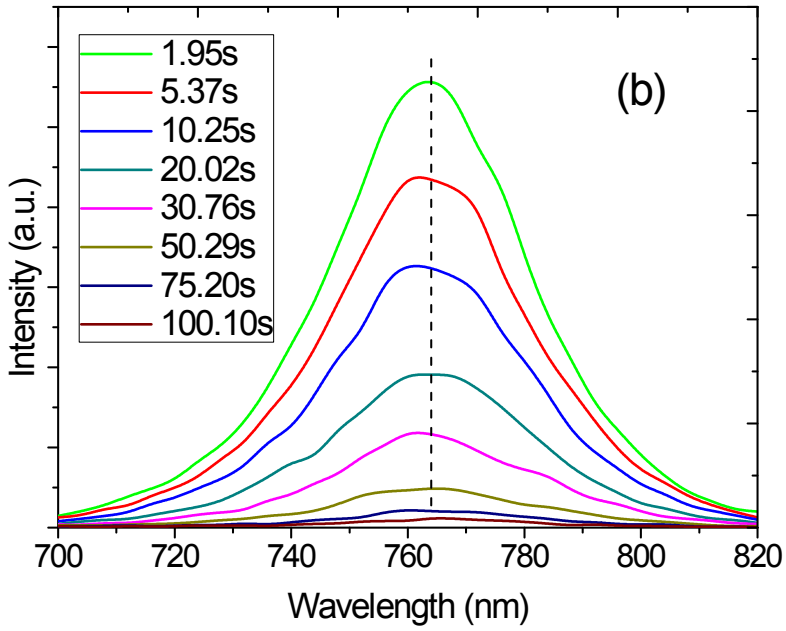


Fig.S2 XPS of VBM for Sample A and B. There is an obvious energy shift 0.17eV between the VBM of Sample A and B. The VBM is determined by linearly extrapolation (blue line).

3. Steady and transient PL of Sample B.


(a)
#A
#B
I_A/I_B=3
PL Intensity (Counts)
650
700
750
800
Wavelength (nm)


(b)
1.95s
5.37s
10.25s
20.02s
30.76s
50.29s
75.20s
100.10s
Intensity (a.u.)
700
720
740
760
780
800
820
Wavelength (nm)

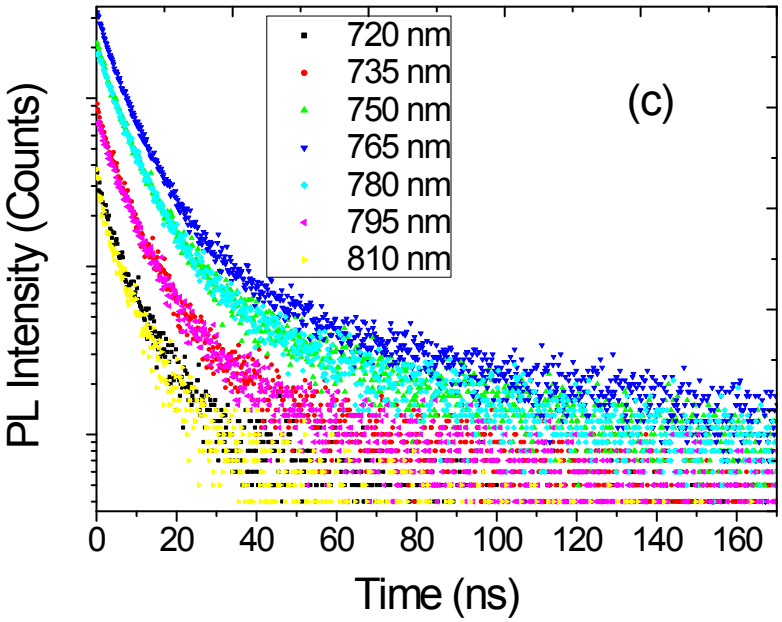


Fig.S3 (a) PL intensity comparison for Sample A and B excited by a 405 nm pulsed laser. Sample A shows a higher integrated PL intensity than Sample B by a factor of 3. "I" in Fig. 4(a) denotes the integrated PL intensity. (b) Time resolved PL of Sample B. After excitation by the 405 nm laser pulse, PL band shows a homogeneous decrease without energy shift. Besides, PL intensity is symmetric on both sides of central wavelength (765 nm). (c) TRPL of wavelength dependence of Sample B. It is obviously that PL from Sample B has homogeneous PL dynamics across the whole PL band. It is thus expected that rich iodine in $MAPbI_3$ does not introduce radiative electronic states within the bandgap.

4. Effects of PMMA Coverage on Sample B.

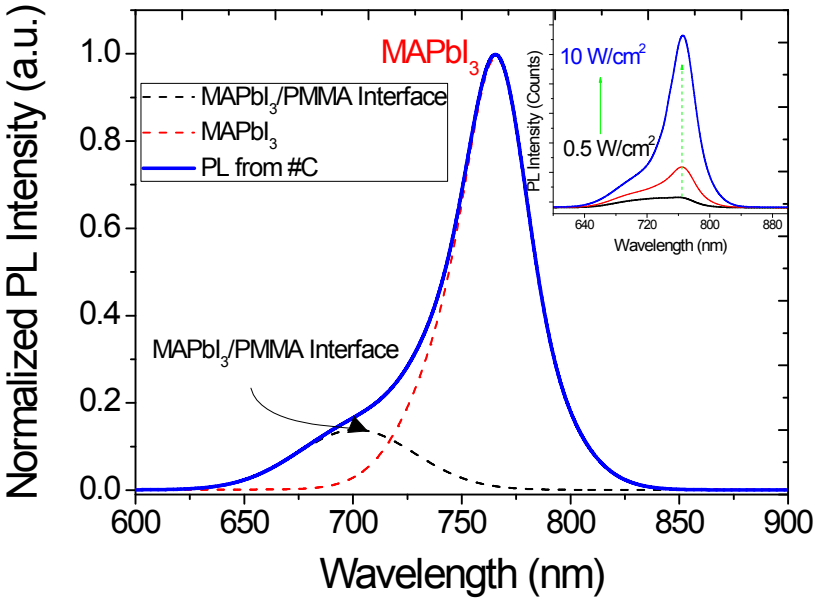


Fig.S4 PL of Sample C excited by the 405 nm laser with intensity of 10 W/cm^2. Through Gaussian deconvolution, two PL components are obtained. As the power of excitation increases from 0.5W/cm^2 to 10W/cm^2 as shown in the inset, PL from the bulk $MAPbI_3$ gets greatly enhanced due to the small density of surface electronic states. The PL feature centered at around 700 nm is from the interface between $MAPbI_3$ and PMMA due to the chemical reaction between $MAPbI_3$ and PMMA.

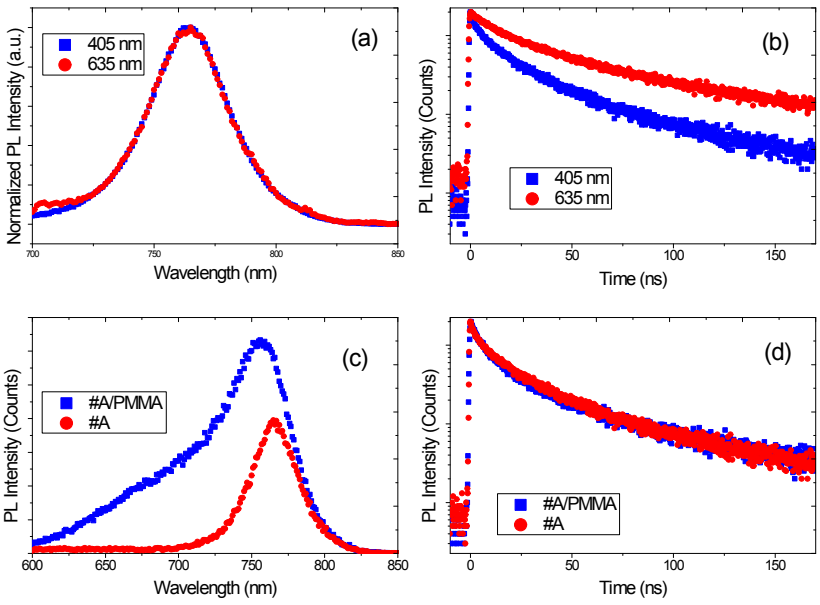


Fig.S5 (a) Normalized PL spectra from Sample A under excitation of the 405 and 635 nm pulsed laser, respectively. (b) PL decay spectra of Sample A under excitation of 405 and 635 nm laser, respectively. It is clearly shown that the 405 nm laser induced a faster PL decay than the 635nm laser. This behavior is quite different from Sample B as discussed in the main text. Since PL excited by the 405nm laser are mainly from the surface of $MAPbI_3$, whereas PL excited by the 635 nm laser is dominated by the interior region of $MAPbI_3$, the comparison of the PL decays in Fig.3(b) (main text) suggests that carriers in $MAPBI_3$ bulk have a longer lifetime than those near the surface region. (c) PL spectra from Sample A before (red) and after (blue) being passivated by PMMA excited by a 405 laser. (d) PL decay spectra at 765 nm of Sample A before (red) and after (blue) being passivated by PMMA. PMMA passivation of Sample A, i.e., the passivation of Pb dangling bonds does not have significance on PL decays. It is thus concluded that the passivation effect of PMMA mainly occurs on I-terminations, and has nothing to do with Pb dangling bonds.

References:

1. Y. Yamada, T. Nakamura, M. Endo, A. Wakamiya and Y. Kanemitsu, *Applied Physics Express*, 2014, **7**, 032302.

2. Y. Yamada, T. Nakamura, M. Endo, A. Wakamiya and Y. Kanemitsu, *IEEE J. Photovolt.*, 2015, **5**, 401-405.