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

Valence Band Dispersion Measurements of Perovskite Single Crystal with Angle-resolved Photoemission Spectroscopy

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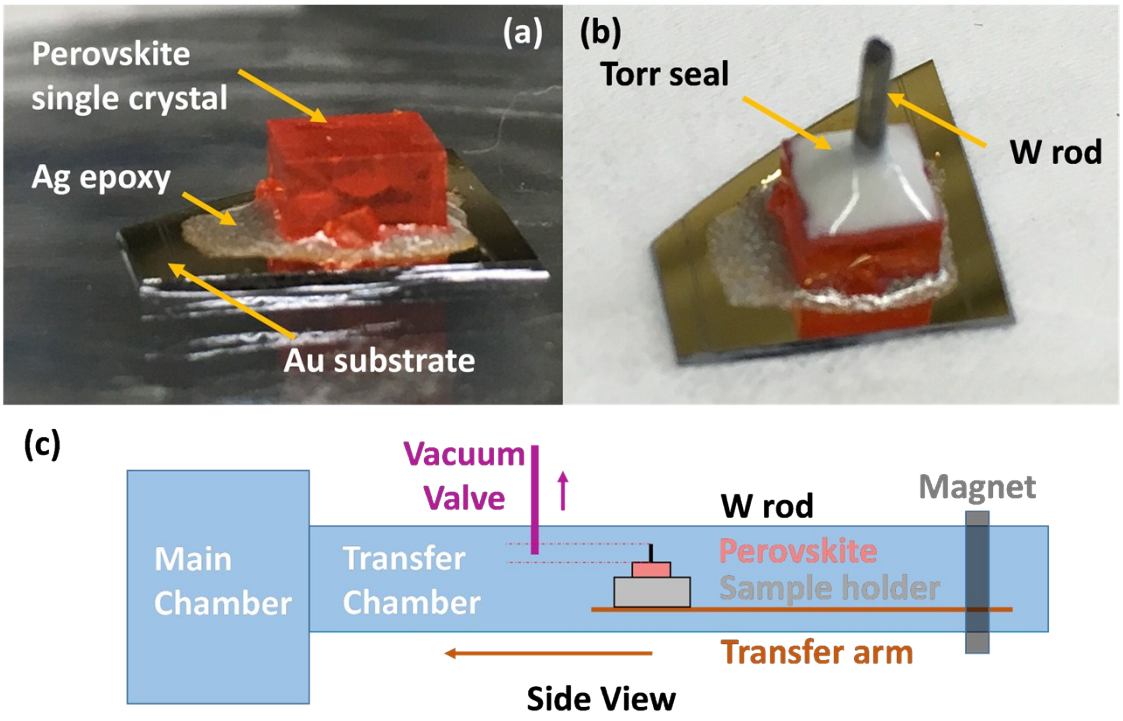

Fig. S1. Detailed schematics of *in-situ* sample cleavage. (a) The perovskite single crystal was glued on top of Au-coated silicon wafer by silver epoxy. (b) A tungsten rod was glued perpendicularly on top of perovskite surface by Varian Torr seal. (c) The sample was cleaved *in-situ* before transferred into main vacuum chamber.

For Angle-resolved photoemission spectroscopy (ARPES) study, one key requirement is to have clean and well defined surfaces. Therefore, we invented this unique cleaving technique to acquire high quality surfaces. As shown in Fig. S1, the perovskite single crystal was first glued on top of Au/Si substrate by silver epoxy (Epoxy Technology, Inc.). Then, a tungsten rod was

glued perpendicularly on top of perovskite surface by Varian Torr seal. After being fixed on the sample holder, the crystal was loaded horizontally into the transfer vacuum chamber with the transfer arm controlled by a magnet. After the chamber was pumped down to ~10^{-6} Torr, the vacuum valve was moved up to a specific height, between the level of the single crystal surface and the tungsten rod tip. The sample was then pushed to the direction of the main chamber. At one particular position, the rod will be hit by the valve, and the top surface of the crystal glued together with it would be cleaved off at the same time. With this method, an *in-situ* cleaved perovskite single crystal (001) surface was achieved. The *ex-situ* cleaving process is about the same, but is processed outside the vacuum chamber.

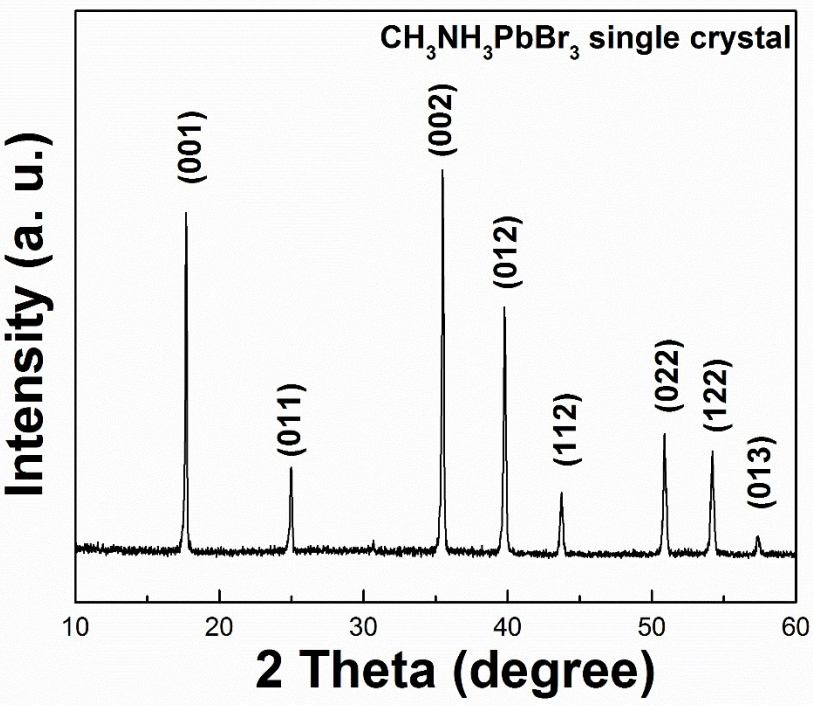

Fig. S2. Powder x-ray diffraction result of $CH_3NH_3PbBr_3$ single crystal with multiple peaks corresponding to a clear cubic structure indexing.

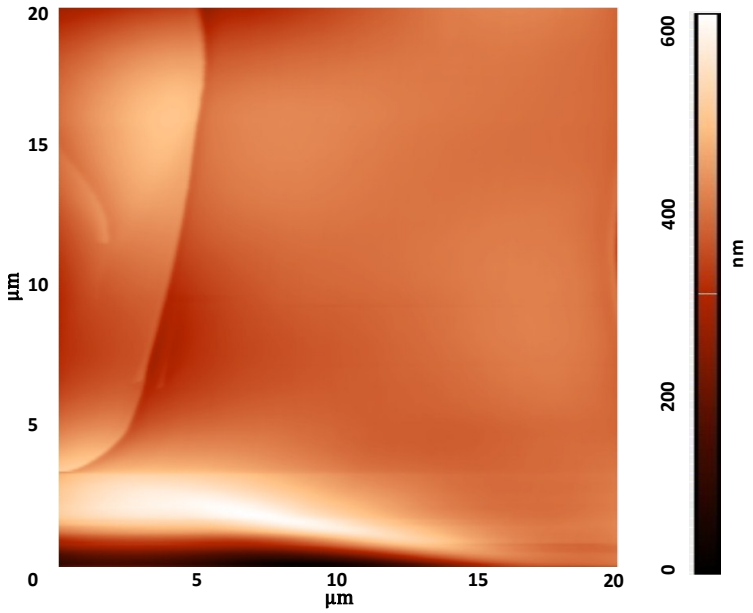

Fig. S3. Two-dimensional atomic force microscopy (AFM) image of the crystal surface at the third position. The image size is 20 µm × 20 µm.

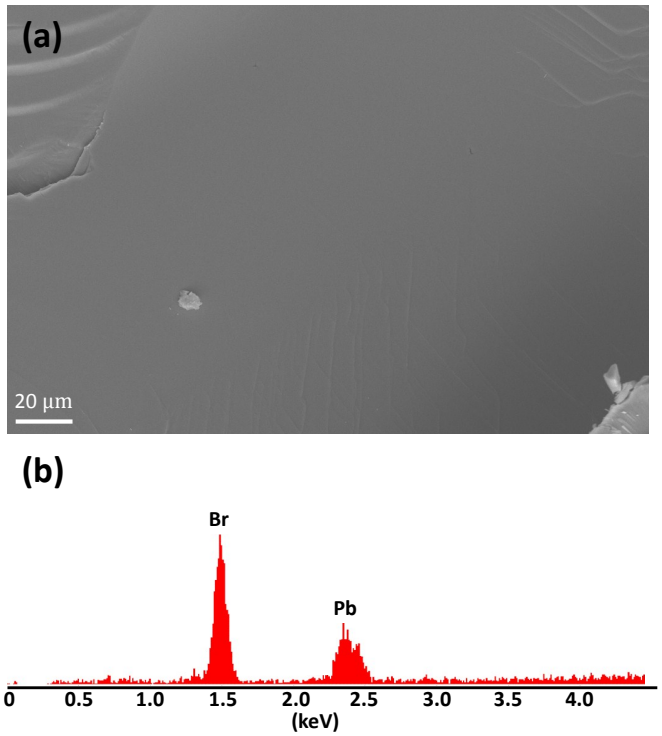

Fig. S4. (a) Scanning electron microscope (SEM) image of the as-cleaved single crystal. (b) Energy dispersive spectroscopy (EDS) for the SEM imaged spot. The applied voltage is 20 KV. It clearly shows the signal of Pb and Br elements from the surface.

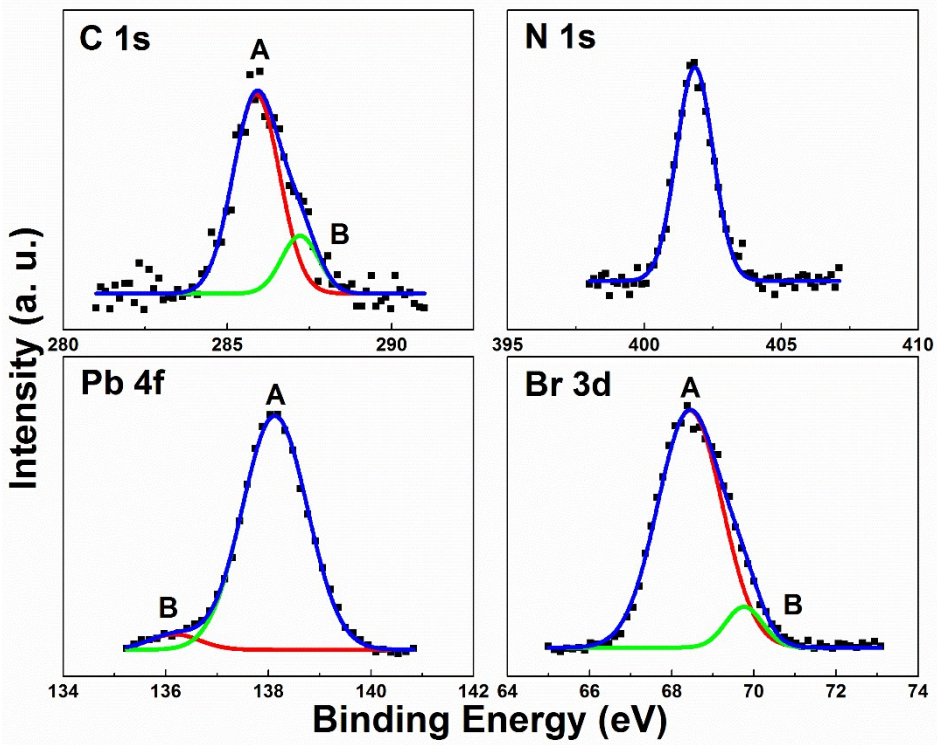

Fig. S5. High resolution x-ray photoelectron spectroscopy (XPS) of the $CH_3NH_3PbBr_3$ single crystal. The C 1s-A peak is from perovskite, while the C 1s-B may be from the residual solvents, such as N, N-dimethylformamide (DMF) and dichloromethane (DCM), used during the crystal growth process. There is only one N 1s peak, indicating that the N 1s in DMF has the same binding energy as the N 1s in perovskite. The Pb 4f-A peak is from perovskite, while the Pb 4f-B peak is metal lead that may come from $PbBr_2$. The Br 3d-A is from perovskite, while Br 3d-B may come from $PbBr_2$. The O 1s peak is not shown here.

We obtained the areas of the XPS spectra of these elements by fitting Gaussian peaks after removing the secondary electron background, followed by normalization with corresponding atomic sensitivity factors. Therefore, the atomic ratio of perovskite single crystal is defined to be C: N: Pb: Br: O = 1.46: 1.05: 1.02: 3.04: 0.05, if taking the area of Pb 4f-A as the basis (the extra 0.02 is from Pb 4f-B). The ratio may suggest that the surface has $CH_3NH_3PbBr_3$: DMF: DCM: $PbBr_2$= 1: 0.05: 0.31: 0.02 as listed in Table S1.

Table S1. Atomic Ratio of $CH_3NH_3PbBr_3$ Single Crystal.

Element	C	N	Pb	Br	O
$CH_3NH_3PbBr_3$	1	1	1	3	0
DMF	0.15	0.05	0	0	0.05
DCM	0.31	0	0	0	0
$PbBr_2$	0	0	0.02	0.04	0
Total	1.46	1.05	1.02	3.04	0.05