

Electronic Supplementary Information for
In Situ Growth of All-Inorganic Perovskite Nanocrystals on Black
Phosphorus Nanosheets

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Experimental details

Materials

The bulk BP crystals were purchased from MoPhos Technology Co. Ltd. (China). Chloroform (CHCl₃) was purchased from Shanghai Lingfeng Chemical Reagent Co. Ltd. (Shanghai, China), Cs₂CO₃ (99.99%), PbO (99.9%), (OA) and tetrabutylammonium bromide (TBAB, 99.0%) were obtained from Aladdin Ltd. (Shanghai, China).

Preparation of micrometer-scale BP sheets

The BP sheets were prepared by a modified liquid exfoliation method according to our previous work.¹ In brief, 20 mg of bulk BP crystal was ground in a mortar with 2 mL of chloroform (CHCl₃) for 10 min in a glovebox (Argon). The mixture was then added to 18 mL of CHCl₃ in a 50 mL glass tube. The tube and sonicator tip were firmly sealed with Teflon tapes. The sample was ultrasonically treated for 3 h at a power of 720 W. Afterwards, the solution was centrifuged for 5 min at 300 rpm and the supernatant containing micrometer-scale BP sheets was collected.

Synthesis of Cs-oleic and Pb-oleic precursor

The Cs-oleic and Pb-oleic precursor was prepared according to the process reported previously.² 0.1629 g (0.5 mmol) of Cs₂CO₃ and 0.2232 g (1 mmol) of PbO were mixed with 5 mL of oleic acid (OA) in a 20 mL glass vial. The mixture was placed on a hot plate at 160 °C and stirred vigorously until a transparent solution was formed. Afterwards, the solution was diluted to 10 mL by adding 5 mL of CHCl₃.

Synthesis of CsPbBr₃ quantum dots and CsPbBr₃-BP hybrid

The Br precursor solution was prepared by mixing 0.0644 g (0.2 mmol) of tetrabutylammonium bromide (TBAB), 1 mL of OA, and 4 mL of CHCl₃. In the synthesis of CsPbBr₃ quantum dots, 1 mL of the Cs and Pb precursor was further diluted with 15 mL of CHCl₃ and 2.5 mL of the Br precursor were added quickly to the diluted solution under vigorously stirring for 10 s. The solution turned transparent green and the CsPbBr₃ quantum dots were synthesized. In the synthesis of the **CsPbBr₃-BP** hybrid, 1 mL of the Cs and Pb precursor was mixed with 7.5 mL of BP sheets (in CHCl₃) and 7.5 mL of CHCl₃. The mixture was stirred for 5 min. Then 2.5 mL of the Br precursor were added quickly under vigorous stirring for 10 s. The solution became yellow-green and the **CsPbBr₃-BP** hybrid were synthesized.

Characterization

The TEM and HR-TEM images were obtained on the FEI Tecnai G2 F30 transmission electron microscope at an acceleration voltage of 200 kV and the SEM images were acquired from the ZEISS SUPRA 55 (Carl Zeiss, Germany) field-emission scanning electron microscope. The UV–vis–NIR absorption spectra were recorded on a Lambda25 spectrophotometer (PerkinElmer) using QS-grade quartz cuvettes at room temperature. The PL spectra were acquired on a fluorescence spectrophotometer (Hitachi F-4600, Japan) and the fluorescence images were recorded on the Olympus-BX63 fluorescence microscope. For the atomic force microscope (AFM) measurement, the as-prepared BP sheets were drop casted on a Si/SiO₂ substrate and dried at 37 °C. The AFM measurement was performed on the Bruker Dimension Icon atomic force microscope (Bruker Corporation, USA) using the tapping mode. The PL lifetime was measured on the Leica SP5 confocal microscopy FLIM (fluorescence lifetime imaging microscopy) system with a 100 × air objective lens (NA = 0.95). A femtosecond pulsed laser with a wavelength of 408nm was used in PL excitation. Photon detection was conducted on

an avalanche photodiode and a synchronous time-correlated single photon counting (TCSPC) module. A high-resolution FLIM areas of $\sim 6 \mu\text{m}^2$ containing sufficient CsPbBr₃ NCs off and on BP sheets were used to perform the statistical analysis for the PL lifetime. The measured PL decay curves were fitted with a bi-exponential function of time (t):

$$I(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right)$$

Where τ_i represents the decay time of i th component and A_i is the amplitude of the i th component. The average lifetime τ_{ave} was estimated from the fitted data according to the equation:

$$\tau_{ave} = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i}$$

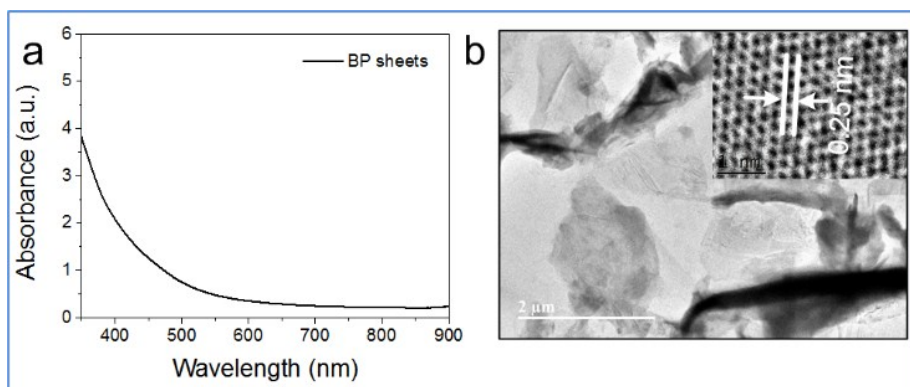


Fig. S1 a) Absorption spectrum of the synthesized BP sheets; b) TEM image and HR-TEM image (inset) of the BP sheets.

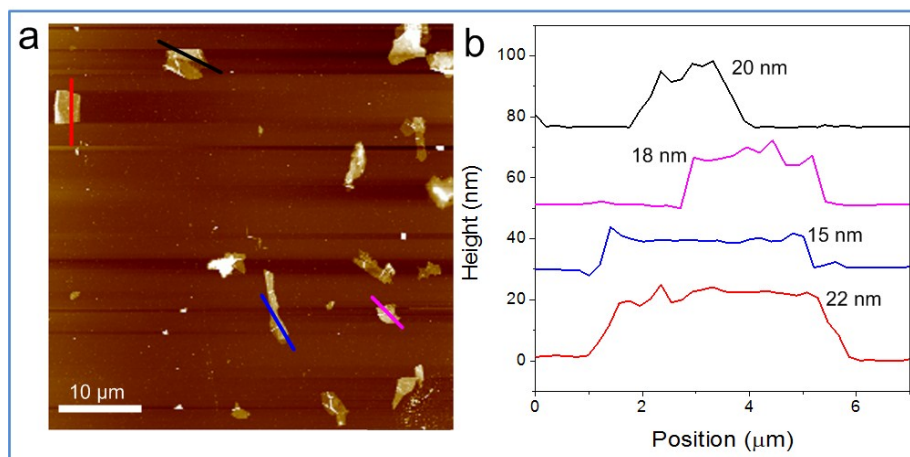


Fig. S2 a) AFM image of as-prepared BP sheets; b) Corresponding height profile of BP sheets

highlighted in a.

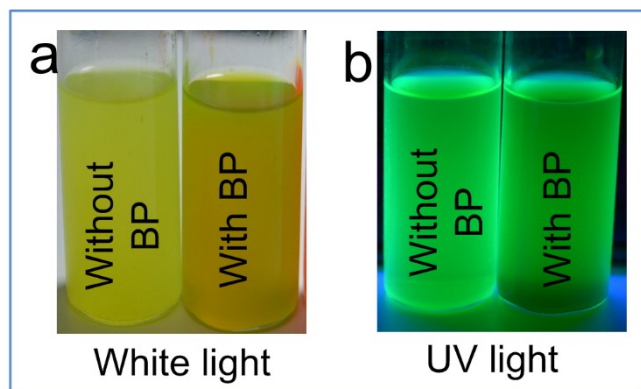


Fig. S3 a) White light and b) UV light images of CsPbBr_3 NCs prepared with and without participation of BP sheets.

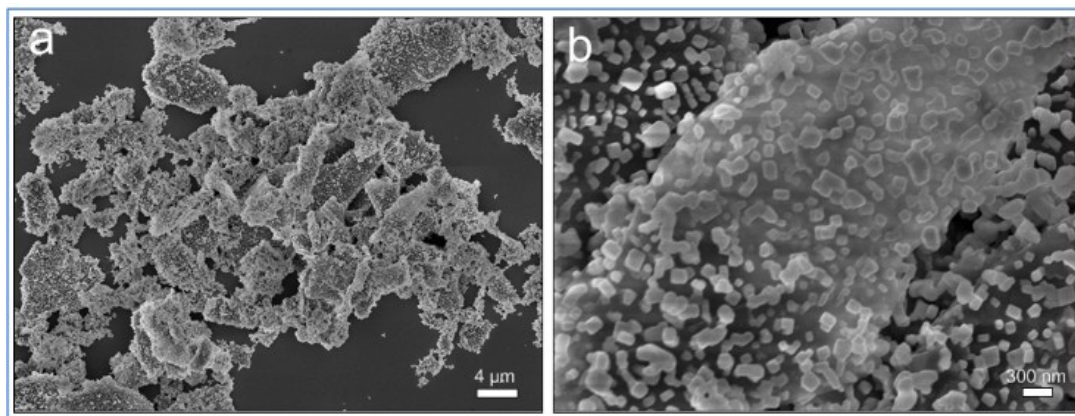


Fig. S4 a) Large scale SEM image of the CsPbBr_3 -BP hybrid; b) Magnified SEM image of one CsPbBr_3 -BP hybrid.

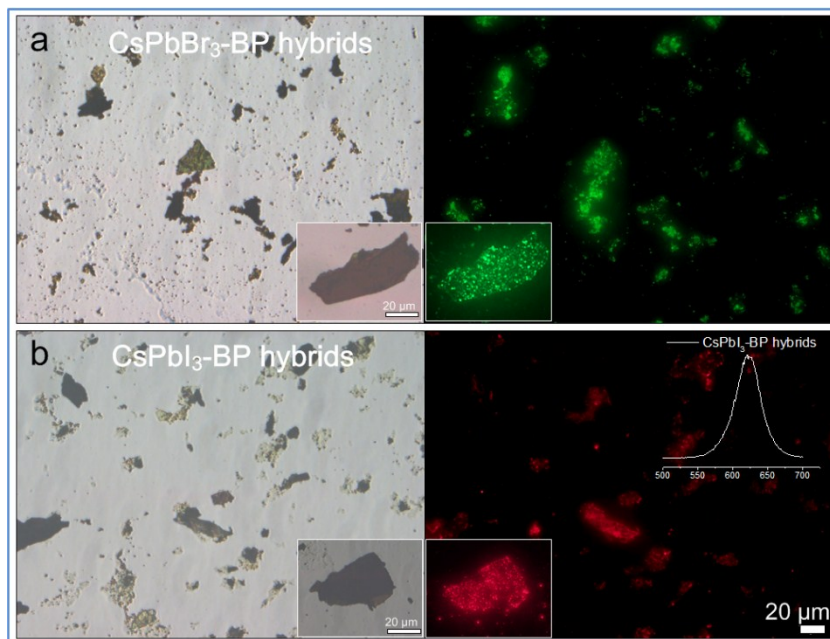


Fig. S5 a) Optical microscopy and PL images of CsPbBr₃-BP hybrid with single CsPbBr₃-BP hybrid inset; b) Optical microscopy and PL images of CsPbI₃-BP hybrid with single CsPbI₃-BP hybrid and PL spectrum inset.

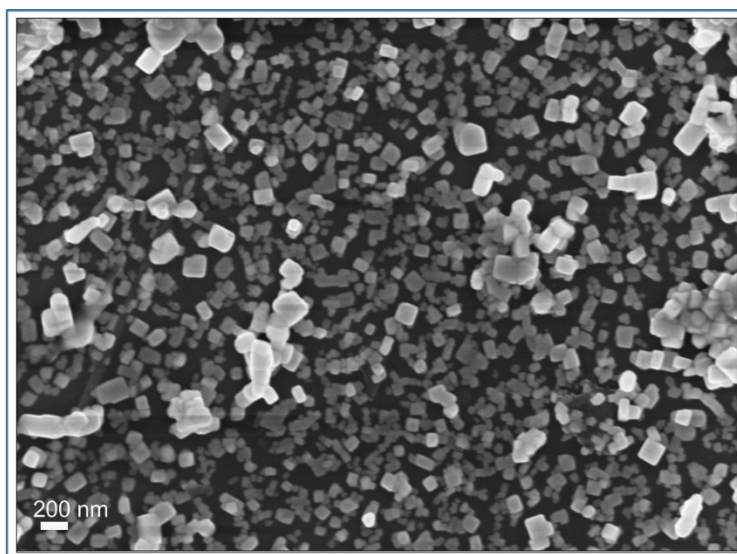


Fig. S6 SEM image of CsPbBr₃ NCs off the BP sheets.

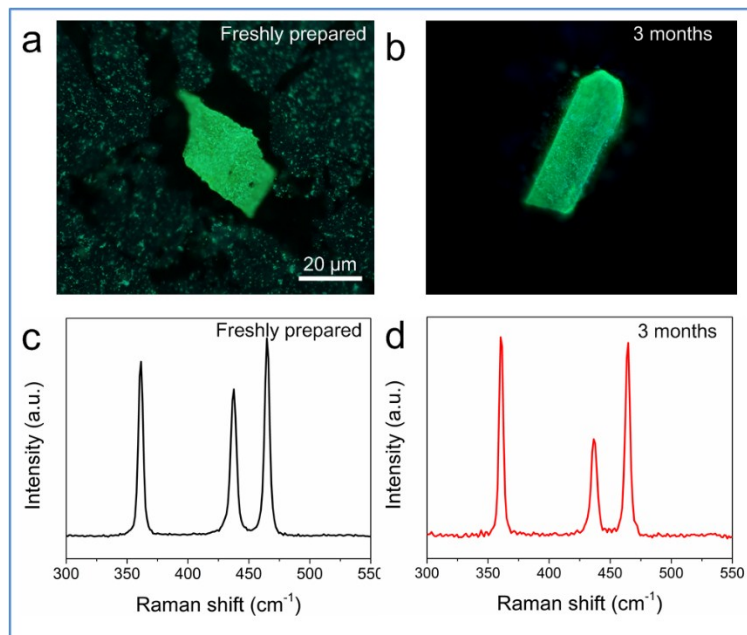


Fig. S7. Fluorescence images of CsPbBr₃-BP hybrid which are a) freshly prepared and b) stored under ambient condition for 3 months; Raman spectra of CsPbBr₃-BP hybrid which are c) freshly prepared and d) stored under ambient condition for 3 months.

References

- 1 H. Huang, Q. Xiao, J. Wang, X.-F. Yu, H. Wang, H. Zhang and P. K. Chu, *npj 2D Mater. Appl.*, 2017, **1**, 20.
- 2 S. Wei, Y. Yang, X. Kang, L. Wang, L. Huang and D. Pan, *Chem. Commun.*, 2016, **52**, 7265-7268.