Electronic Supplementary Information

Electrochemical Synthesis of Colloidal Lead- and Bismuth-based Perovskite Nanocrystals

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Experimental Section

Materials. Lead foil (Pb, 5.25 cm × 0.75 cm × 0.25 cm), oleic acid ($C_{18}H_{33}COOH$, OA, tech. grade, 90%), oleylamine (OAm, 80-90%), methylamine (CH_3NH_2, 40 wt % in water), hydroiodic acid (HI, ≥47.0% in water), hydrobromic acid (HBr, 48 wt %, in water), n-butanol (C_4H_9OH, BuOH, >99.5%), n-octanoic acid ($C_7H_{15}COOH$, OcA, 99%) were purchased from Aladdin Inc. Bismuth plate (Bi, 5.25×0.75×0.25 cm) was purchased from Xingye Metal Material Co. Ltd (Hebei). Graphite (C, 99.99%, 5.25×0.75×0.25 cm) was purchased from Jinglong Carbon Technology Co. Ltd (Beijing). Toluene, chloroform, ethanol, and acetone were obtained from Guangzhou Chemical Reagent Inc. Tetraoctylammonium bromide (TOABr, 98%) and was purchased from Sigma-Aldrich Inc. Sodium oleate ($C_{18}H_{33}COONa$, NaOA, 98%) was purchased from Ailan Chemical Technology Co. Ltd (Shanghai). All chemicals were used as received without any further purification.

CH_3NH_3Br Synthesis. MABr was synthesized following a published method.[1] 10.82 mL (0.126 mol) of methylamine was added to a 50-mL round-bottom flask. 10 mL of HBr in water was added dropwise into the flask under vigorous magnetic stirring. The container was soaked in an ice bath and the reaction lasted for 2 h. After the reaction, most of the solvent was evaporated using a rotary evaporator. The powdery product was separated by pressure-reduced filtration and washed by 3~5 mL of ethyl ether for more than 3 times. After drying in a vacuum oven at 60°C for 5 h, the resulting salt powders were transferred in a 20-mL vial and stored in a desiccator for further use.

CH_3NH_3I Synthesis. MAI was synthesized following a published method.[1] 10.82 mL

(0.126 mol) of methylamine was added to a 50-mL round-bottom flask. 10~20 mL of HI in water was added dropwise into the flask under vigorous magnetic stirring. The container was soaked in an ice bath and the reaction lasted for 2 h. After the reaction, most of the solvent was evaporated using a rotary evaporator. The powdery product was separated by pressure-reduced filtration and washed by 3~5 mL of ethyl ether for more than 3 times. After drying in a vacuum oven at 60°C for 5 h, the resulting salt powders were transferred in a 20-mL vial and stored in a desiccator for further use.

Preparation of Precursor Solutions. 11.2 mg of MABr or 15.8 mg MAI (0.1 mmol) was fully dissolved in 2 mL of BuOH in a 20-mL vial. Both solutions were heated at 80°C in air for 1 h, and cooled down naturally to room temperature to form the MABr (MAI) /BuOH precursor solution. 31.6 mg of MAI (0.2 mmol) was fully dissolved in a mixed solvent including 12 mL of $CHCl_3$ and 5 mL of BuOH at 90°C for 1h to form MAI/ $CHCl_3$/ BuOH solution. 54.7 mg of TOABr (0.1 mmol) was weighted out and dissolved in a mixed solvent (including 5 mL of OA (OcA or OAm) and 5 mL of toluene) in a 20-mL vial at room temperature to form the TOABr/OA (OcA or OAm)/toluene solution. 5 mL of toluene and 5 mL of OcA were mixing in a 20-mL vial at room temperature to form the OcA /toluene solution. 30 mg NaOA was fully dissolved in 600 μL OcA to form the NaOA/OcA ligand solution at 75°C for 0.5 h.

EC Synthesis of $CH_3NH_3PbBr_3$ NCs. The EC reactions were carried out in the electrolysis cell of IKA® ElectraSyn 2.0 (Figure S1). Before each experiment, the lead and graphite electrodes were polished using sand paper and cleaned by ethanol or acetone. The precursor solutions of MABr/BuOH (1.5 mL), TOABr/OA/toluene (1.5 mL), and TOABr/OAm/toluene (0.05 mL) were added in the 5-mL reaction vial equipped with a

magnetic stir bar. The vial was attached to the vial cap equipped with electrodes as shown in Figure S1. The EC reaction was carried out at room temperature in air with continuous stirring under a constant current of 5 mA. After 5 min, the cap was removed and the product was isolated from the solution to by the centrifugation at 8000 rpm for 2 min. The supernatant was decanted, and the precipitate was redispersed in hydrophobic organic solvents (e.g. chloroform, toluene, hexane) for further use. It is important to note that the longer reaction time would cause the overgrow of the PNCs (sizes over 1 μm) and the product particles were not re-dispersible in the clean hydrophobic solution after centrifugation.

EC Synthesis of $CH_3NH_3PbI_3$ NCs. The EC reactions were carried out in the electrolysis cell of IKA® ElectraSyn 2.0 (Figure S1). Before each experiment, the lead and graphite electrodes were polished using sand paper and cleaned by ethanol or acetone. The precursor solutions of MAI/BuOH (1.0 mL), OcA/ toluene (1.0 mL), and OAm/ toluene (0.1 mL) were added in the 5-mL reaction vial equipped with a magnetic stir bar. The vial was attached to the vial cap equipped with electrodes as shown in Figure S1. The EC reaction was carried out at room temperature in air with continuous stirring under a constant current of 5 mA. After 10 min, the cap was removed and the product was isolated from the solution to by the centrifugation at 8000 rpm for 2 min. The supernatant was decanted, and the precipitate was redispersed in hydrophobic organic solvents (e.g. chloroform, toluene, hexane) for further use. Similar to the synthesis of $CH_3NH_3PbBr_3$ NCs. The longer reaction time would cause the overgrow of the PNCs and the product particles were not re-dispersible in the clean hydrophobic solution after centrifugation.

EC Synthesis of Mixed-Halide PNCs. The EC reactions were carried out in the

electrolysis cell of IKA® ElectraSyn 2.0 (Figure S1). Before each experiment, the lead and graphite electrodes was polished using sand paper and cleaned by ethanol or acetone. The precursor solutions of MAI/BuOH (0.1~1.0 mL), MABr/BuOH (0.1~1.0 mL), TOABr/OcA/ toluene (1.0 mL), and OAm/ toluene (0.020 mL~0.1 mL) were added in the 5-mL EC reaction vial equipped with a magnetic stir bar. The vial was attached to the vial cap equipped with electrodes as shown in Figure S1. The EC reaction was carried out at room temperature in air with continuous stirring under a constant current of 5 mA. After 10 min, the cap was removed and the product was isolated from the solution to by the centrifugation at 8000 rpm for 2 min. The supernatant was decanted, and the precipitate was redispersed in hydrophobic organic solvents (e.g. chloroform, toluene, hexane) for further use.

EC Synthesis of $(CH_3NH_3)_3Bi_2Br_9$ NCs. The EC reactions were carried out in the electrolysis cell of IKA® ElectraSyn 2.0 (Figure S1). Before each experiment, the bismuth and graphite electrodes were polished using sand paper and cleaned by ethanol or acetone. The precursor solutions of MABr/BuOH (3.0 mL), and OA (0.1 mL) were added in the 5-mL EC reaction vial equipped with a magnetic stir bar. The vial was attached to the vial cap re-equipped with Bi and graphite electrodes. After that, The EC reaction was carried out at room temperature in air with continuous stirring under a constant current of 100 mA. After 20~30 min, the cap was removed and the product was isolated from the solution to by the centrifugation at 8000 rpm for 2 min. The supernatant was decanted, and the precipitate was redispersed in hydrophobic organic solvents (e.g. chloroform, toluene,) for further use.

EC Synthesis of $(CH_3NH_3)_3Bi_2I_9$ NCs. The EC reactions were carried out in the

electrolysis cell of IKA® ElectraSyn 2.0 (Figure S1). Before each experiment, the bismuth and graphite electrodes were polished using sand paper and cleaned by ethanol or acetone. The precursor solutions of MAI/ $CHCl_3$/ BuOH (3.0 mL) and NaOA/OcA (0.6 mL) were added in the 5-mL EC reaction vial equipped with a magnetic stir bar. The vial was attached to the vial cap re-equipped with Bi and graphite electrodes. After that, The EC reaction was carried out at room temperature in air with continuous stirring under a constant current of 100 mA. After 1 h, the cap was removed and the product was isolated from the solution to by the centrifugation at 8000 rpm for 2 min. The supernatant was decanted, and the precipitate was redispersed in hydrophobic organic solvents (e.g. chloroform, toluene) for further use.

Absorption and photoluminescence (PL) measurements. The absorption spectra were taken on a Shimadzu UV3600 spectrometer. Samples were prepared by the dilution of the PNC solutions in hexane or chloroform in a standard quartz cuvette (path length: 1 cm). PL spectra of the PNC solutions were recorded using an FLS 980 spectrometer (Edinburgh Instruments).

Powder X-ray diffraction (XRD) analysis. XRD patterns were obtained using a Rigaku Miniflex 600 diffractometer with a NaI scintillation counter and using monochromatized Cu-Kα radiation (1.5406 Å) with operating at 45 kV and 15 mA. The samples were prepared by drop casting a concentrated solution on glass piece and measured in air at room temperature.

Raman and Fourier Transform infrared spectroscopy (FT-IR). Raman spectroscopy was performed using an Ocean Optics QE Pro Raman spectrometer equipped with a 784.9 nm pulse laser on the powdery sample. FT-IR measurements were carried out in solutions

with Frontier FT-IR Spectrometer (ATR mode). Samples were redispersed in hexanes, and subsequently transferred onto the holder by drop-casting, and dried at room temperature under air atmosphere before the measurement.

Transmission electron microscopy (TEM). TEM images were acquired on a JEOL JEM-2010HR microscope operated at 200 kV accelerating voltage. Samples were prepared by drop casting diluted NC suspensions onto TEM grids (200-mesh, carbon-coated copper grid).

X-ray photoelectron spectroscopy (XPS). XPS measurements were performed by using a Thermo Scientific KAlpha XPS system. Samples were redispersed in hexanes, subsequently transferred onto the glass substrate by drop-casting, and fully dried under vacuum overnight.

Table S1. Materials consumption comparison of the general ABX_3 PNC production using various synthetic approaches (A = MA^+, Cs^+, FA^+, B = Pb^{2+}, X = Cl^-, Br^-, I^-).

Method to prepare 1 mg of PNCs	Hot-injection[2] (Yield: 15-20%)	LARP[3] (Yield: 1-4%)	This work (Yield: 42%)
Precursor usage (mmol)	A-type precursor (1.0×10^{-2}) B-type precursor (1.9×10^{-2})	A-type precursor (8.3×10^{-2}) B-type precursor (1.0×10^{-1})	MABr (4.9×10^{-3}) TOABr (1.0×10^{-3})
Solvent/ligand usage (mL)	ODE (5.3×10^{-1}) OA (5.0×10^{-2}) OAm (5.0×10^{-2})	OA (2.6×10^{-1}) OAm (1.0×10^{-2}) DMF (2.6) toluene (1.4×10)	OA (9.8×10^{-2}) OAm (1.6×10^{-2}) toluene (5.1×10^{-2}) BuOH (4.9×10^{-2})
Overall precursor Usage (mmol)	2.9×10^{-2}	1.8×10^{-1}	5.9×10^{-3}
Overall solvent Usage (mL)	6.3×10^{-1}	1.7×10	2.5×10^{-1}

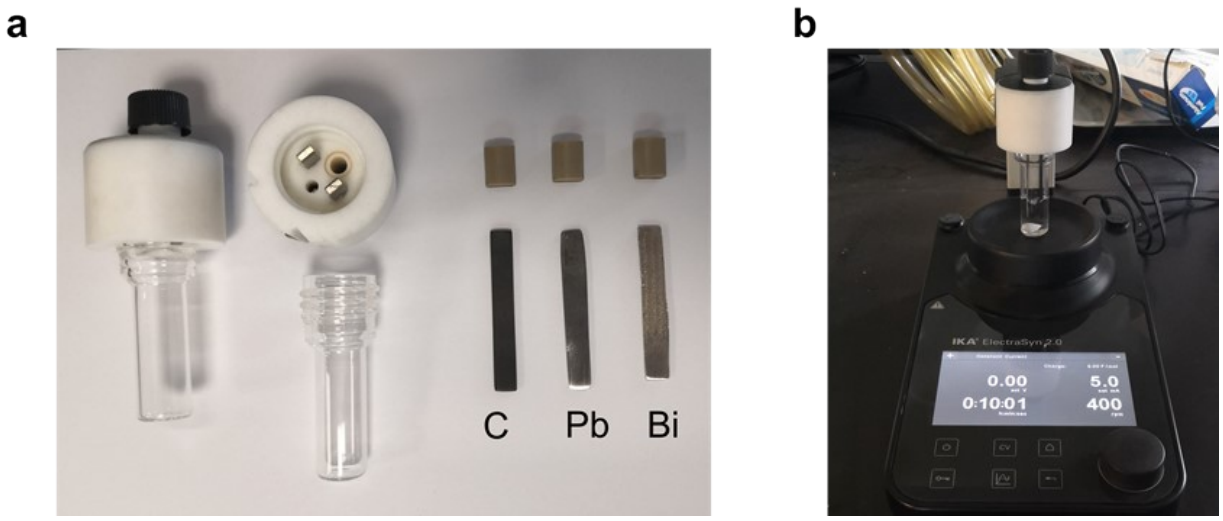

Figure S1. Instrumental setup of the EC synthesis of PNCs. (a) Image of the general components including the electrolysis cell graphite electrode, and the metal foils. (b) The overall setup of IKA® ElectraSyn 2.0 package for the synthesis of PNCs.

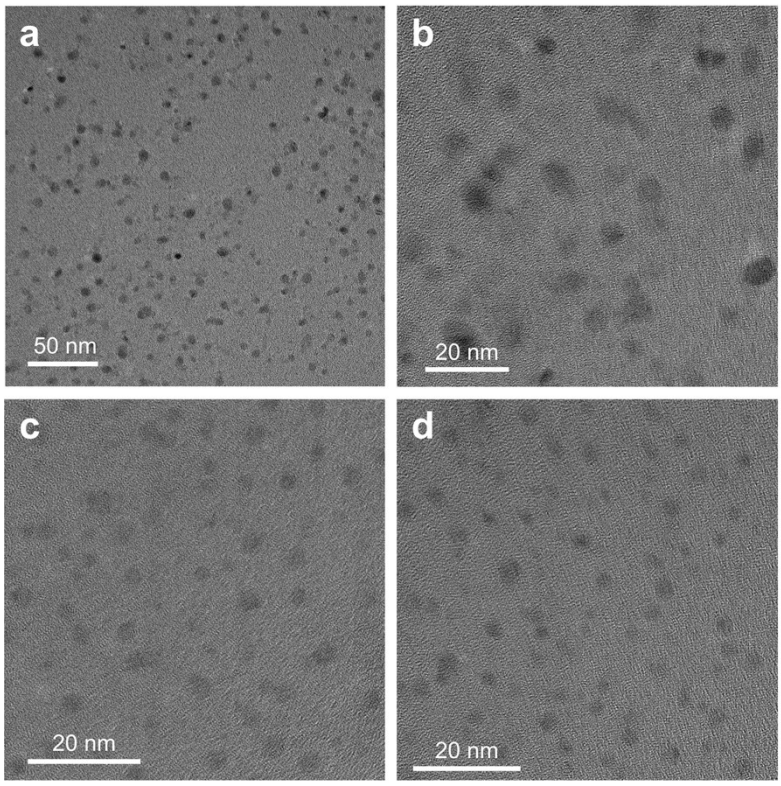

Figure S2. Additional bright-field TEM images of (a, b) $MAPbBr_3$ and (c, d) $MAPbI_3$ PNCs.

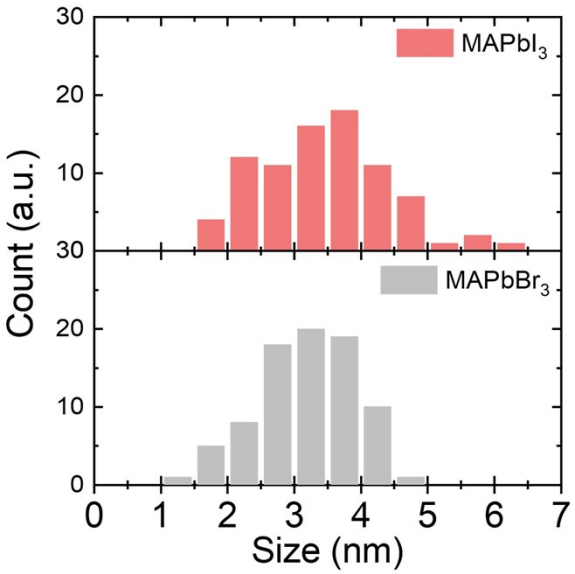

Figure S3. Size distribution of $MAPbBr_3$ and $MAPbI_3$.

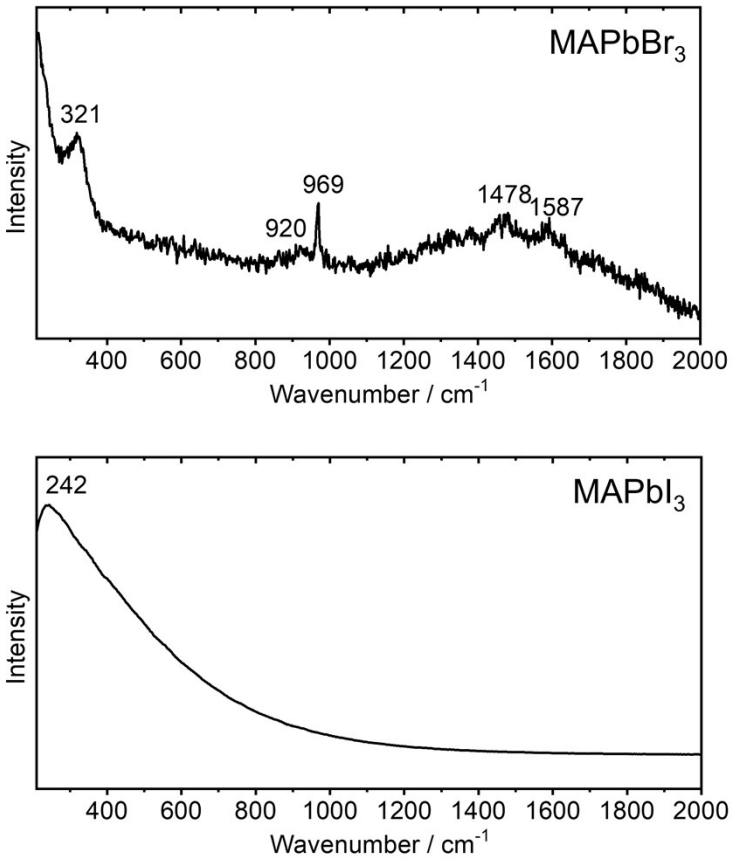

Figure S4. Raman spectra of $MAPbBr_3$ and $MAPbI_3$ PNC powders measured at room temperature under ambient conditions (excitation wavelength: 784.9 nm).

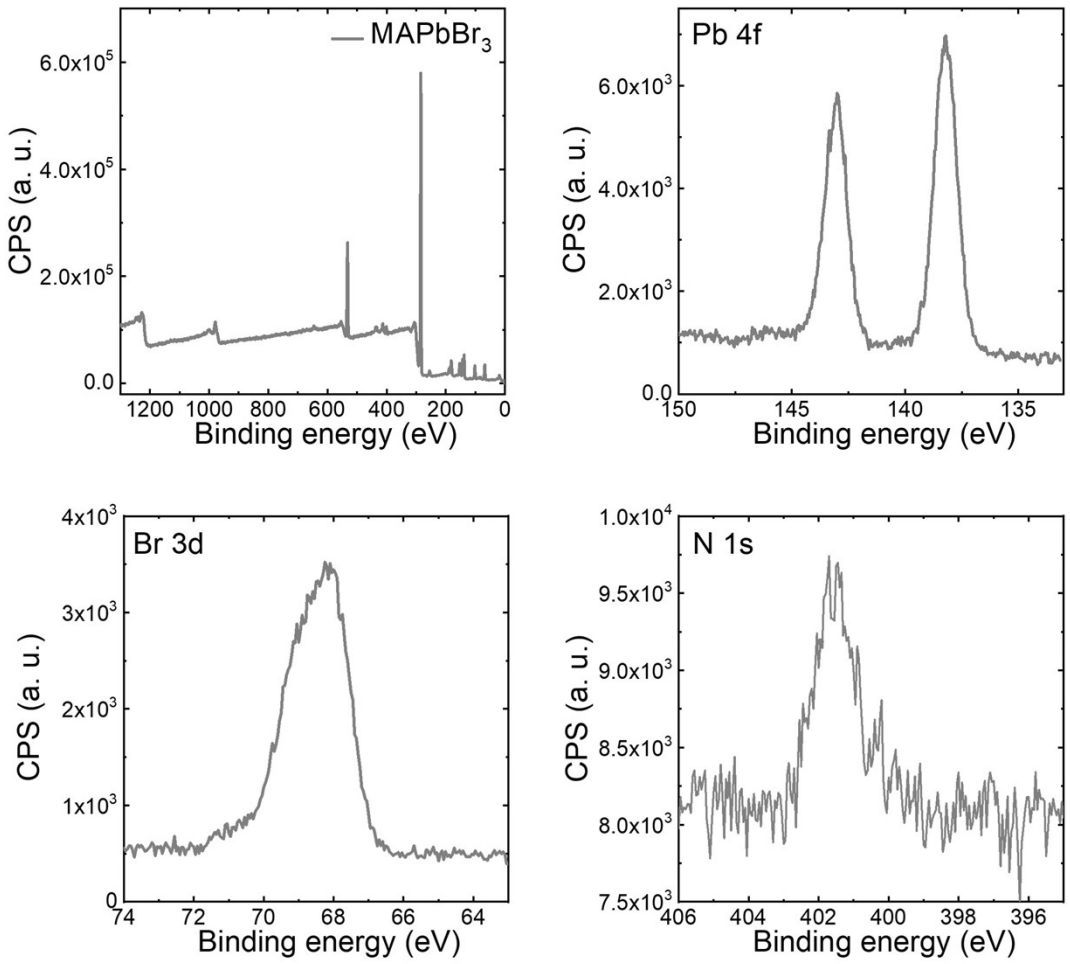

Figure S5. X-ray photoelectron spectra of the purified $MAPbBr_3$ PNC powders. High-resolution XPS analyses further confirmed the elemental composition of PNCs: lead (4f) at 138.2 and 143.1 eV, nitrogen (1s) at 401.9 eV, and bromine (3d) at 68.3 eV.

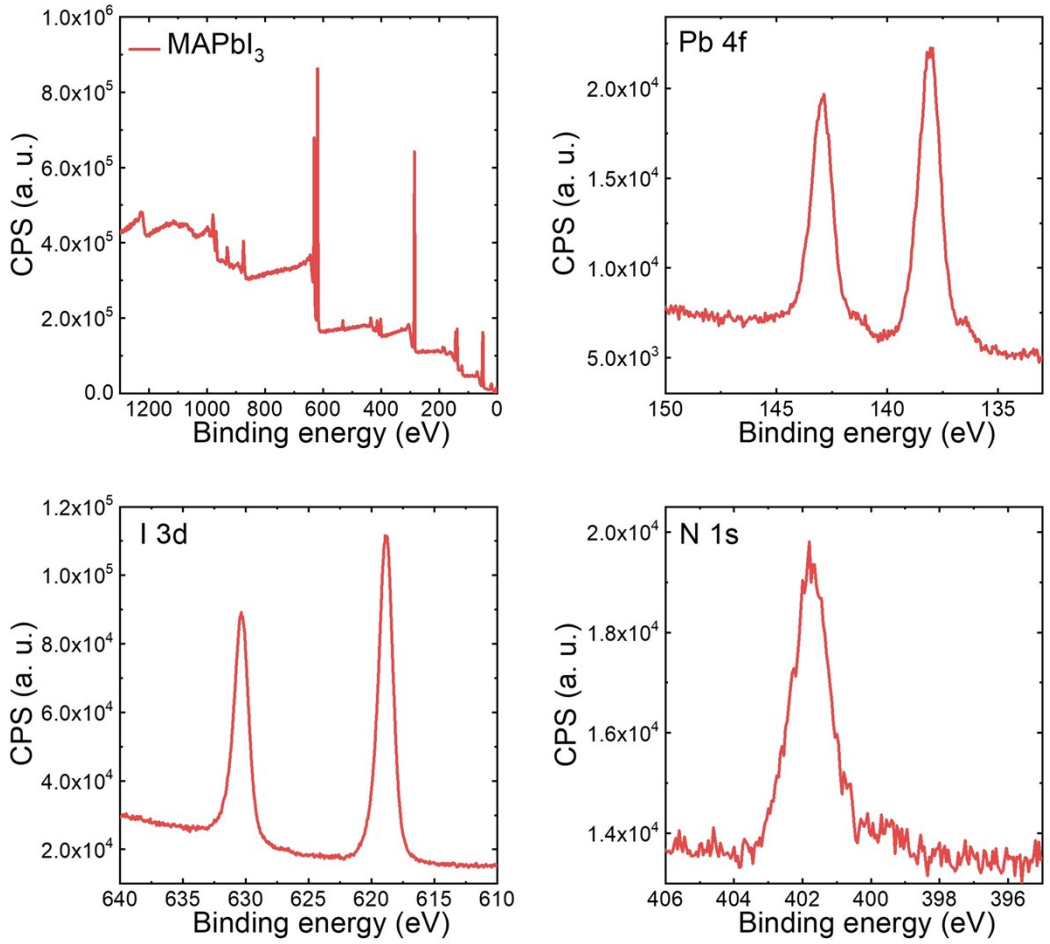

Figure S6. X-ray photoelectron spectra of the purified $MAPbI_3$ PNC powders. High-resolution XPS analyses further confirmed the elemental composition of PNCs: lead (4f) at 138.2 and 143.1 eV, nitrogen (1s) at 401.9 eV, and iodine (3d) at 618.8 and 630.4 eV.

References

1. F. Zhang, H. Zhong, C. Chen, X.-g. Wu, X. Hu, H. Huang, J. Han, B. Zou and Y. Dong, *ACS Nano*, 2015, **9**, 4533-4542.

2. L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh and M. V. Kovalenko, *Nano Letters*, 2015, **15**, 3692-3696.

3. H. Huang, Q. Xue, B. Chen, Y. Xiong, J. Schneider, C. Zhi, H. Zhong and A. L. Rogach, *Angew. Chem. Int. Ed.*, 2017, **56**, 9571-9576.