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Supporting Information

Facet-Controlled Preparation of Hybrid Perovskite Microcrystals in the Gas Phase and the Remarkable

Effect on Optoelectronic Properties

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EXPERIMENTAL DETAILS

Precursor synthesis and aerosol treatment. In a typical synthesis procedure, the precursor with an equivalent stoichiometric ratio of PbBr₂:MABr (1:1) MAPbBr₃TEG₂-eq was produced by subsequently dissolving 550.5 mg PbBr₂ (1.5 mmol) and 168.0 mg MABr (1.5 mmol) 5 mL dry Triethelhylene glycol (TEG) to yield the transparent liquid. For MAPbBr₃TEG₂-ex a molar ratio of PbBr₂:MABr (1:1.3) was utilized, respectively. Both precursors were kept under dry conditions in a nitrogen atmosphere. The solid precursor MAPbBr₃TEG₂ crystallizes out over time but can be dissolved at elevated temperatures of 35 °C. For the aerosol synthesis, 5 mL of the precursor solution MAPbBr₃TEG₂-eq or MAPbBr₃TEG₂-ex were used to generate MAPBr-110 or MAPBr-100 materials, respectively. Therefore, the precursor solution was kept under a nitrogen atmosphere at 35 °C in a reservoir vessel equipped with a suction tube to the aerosol reactor (TSI Inc., model 3076). A constant volumetric nitrogen flow of 2.0 L/min was applied to carry the generated droplets through a tubular oven (length: 65 cm; diameter 2.6 cm) at T= 150 °C. Orange MAPbBr₃ crystals were collected on various substrates (e.g. Si, glass) or with a filter system and analyzed without further purification.

Single Crystal X-ray analysis. MAPbBr₃TEG₂ (1) was recrystallized from the melt, mounted in inert oil and transferred to the cold gas stream of the diffractometer. The crystal structure is deposited on the Cambridge Crystallographic Structural Database (CCSD) with the number 1538521. Single crystal X-ray data was collected on STOE IPDS-II with a graphite monochromator and a Mo-K ∂ x-ray source.

Crystal data. $C_{13}H_{34}Br_{3}NO_{8}Pb$, M = 779.33, orthorhombic, a = 7.7705(5), b = 21.1114(15), c = 29.069(2) Å, U = 4768.7(6) Å³, T = 173 K, space group $-P_{2bc2ac}$ (no.61), Z = 8, 20078 reflections measured, 4977 unique (*R*int = 0.0475), which were used in all calculations. The final wR(F2) was 0.1340 (all data). CCSD number is 1538521.

Aerosol-synthesis. In a typical synthesis, a 0.3 M solution of PbBr₂ and MABr in TEG (dry) was used for the aerosol process. The clear transparent precursor solution was kept at 35°C to prevent the crystallization of solid MAPbBr₃TEG₂. The MAPbBr₃ microcrystals were synthesized by a set-up of an aerosol reactor (TSI Inc., model 3076) at a volumetric flow of 2.0 L/min, followed by an oven (length: 65 cm; diameter 2.6 cm) at T=150 °C. Crystals were collected on various substrates (e.g. Si, glass) or with a filter system.

Additional analytics. In-situ UV/VIS experiments were performed on a Cary 50 equipped with a probe (slit 1 mm). DSC measurements were performed with a Netzsch DSC 204 F1 Phoenix. Powder X-ray diffraction analysis (PXRD) was performed on a Bruker AXS D8 advance diffractometer with a CU-K α source with a Lynxeye XE detector. UV-Vis were acquired on an Agilent Cary 5000 UV-Vis-NIR spectrometer, equipped with an integrated sphere. SEM micrographs were taken on a Zeiss Crossbeam 1540XB equipped with InLens and SE2 detector with an acceleration Voltage of 1-2 kV to prevent damage of MAPbBr₃ caused by the electron beam. Steady state and fluorescence lifetime measurements were performed on a FluoTime 300 from Picoquant equipped with a laser $\lambda_{esc} = 485$ nm (P = 0.62 mW, F = 40 kHz, $P_{\rho} \approx 0.08$ W/cm², $E_{\rho} \approx 2 \mu$ J/cm²). Fluorescence microscopy was performed on a TCS SP5 confocal laser scanning microscope (Leica) using an oil immersion objective lens (63 x, 1.4 NA, HCX PLAPO, Leica) with an laser excitation of 488 nm (CW, $P_{6\%} = 3.2 \mu$ W, $P_{10\%} = 7.3 \mu$ W, $P_{\rho,6\%} \approx 0.84$ W/cm², $P_{\rho,10\%} \approx 1.9$ W/cm²) collecting wavelengths from 510- 600 nm. Wavelength dependent fluorescence microscopy studies were performed with a detection window of 10 nm from 500- 600 nm.

Figure S-1. Differential Scanning Calorimetry Measurement of the crystalline precursor MAPbBr₃TEG₂.



The precursor MAPbBr₃TEG₂ shows a broad melting range between 20-50°C with a maximum $(T_m = 41.6$ °C). The enthalpy of fusion is $\Delta H_{fus} = 23.38$ J/g.





The conversion of the crystalline precursor $MAPbBr_3TEG_2$ (Prec) to the melt (t= 0s) and further conversion at T= 120°C for t= 5 s, 10 s and 60 s. $MAPbBr_3$ reference pattern is indicated by orange bars.

Figure S-3 UV-Vis conversion study of precursor melt with equimolar (MABr:PbBr₂=1:1) and the excess ratio of MABr (MABr:PbBr₂=1.3:1).



UV-Vis trace at λ = 500 nm for the conversion to MAPBr precursor melt in the equimolar ratio (squares) and excess of MABr (triangles) while heating up the precursor from 35°C to 70°C (12°C/min heating rate).

Figure S-4. UV-Vis of precursor melt with equimolar (MABr:PbBr₂=1:1) and the excess ratio of MABr (MABr:PbBr₂=1.3:1).



UV-Vis spectra of the precursor melt in the equimolar ratio (black) and excess of MABr (red) with indicated decrease in absorption tail which is related to long polymeric 1D $(PbBr_3)_n^n$ chains.

Figure S-5. Extracted lattice angles of <110> and <100>-oriented MAPbBr₃ from single crystal X-ray data.



Theoretical lattice angles α and β of MAPbBr₃ in (a) <110> orientation with $\alpha \approx 110^{\circ}$ and $\beta \approx 125^{\circ}$ and (b) <100> orientation with $\alpha \approx 90^{\circ}$ and $\beta \approx 135^{\circ}$. Methyl ammonium cations were removed for clarity.





SEM micrograph of MAPBr-100 microcrystals showing (a) rough (100)-surface as a top view, (b) etched surface along <100> and (c) start of the etching in the center of the cubic MAPBr₃, scale bar $\approx 1 \ \mu m$.

Figure S-7. Detailed PXRD analysis of MAPBr-110 and MAPBr-100.



Gauss fit in black and indicated MAPbBr₃ reference signals in gray bars for the (a) (011)-signal of MAPBr-110 and (b) (001)-signal in MAPBr-100 microcrystals. (c) Table of derived unit cell parameters for <110> and <100> oriented microcrystals.



Figure S-8. Kubelka Munk evaluation of MAPBr-110 and MAPBr-100 from diffuse reflectance UV-Vis spectra.

Bandgap evaluation of MAPBr-110 $E_{gap,<110>}(eV)=2.26$ in blue and MAPBr-100 $E_{gap,<100>}(eV)=2.25$ in red.

Figure S-9. Particle size distribution analysis of MAPBr-110 and MAPBr-100 derived from SEM micrographs (particles were collected on a filter paper in the aerosol process).



SEM micrograph of randomly oriented particles for the evaluation of the size distribution from the aerosol process of (a) MAPBr-110 and (b) MAPBr-100, scale bar $\cong 2 \mu m$. (c) Particle size distribution evaluated from SEM micrographs by counting 200 individual particles of MAPBr-110 (874 nm± 454 nm) in blue and MAPBr-100 (752 nm ± 277nm) in red.

Figure S-10. Wavelength dependent confocal fluorescence spectroscopy analysis at 488 nm laser excitation with a wavelength detection window of 10 nm.



Wavelength dependent stack of confocal spectroscopy images of (a) individual MAPBr-110 particles indicated by blue numbers with particle sizes from 430 nm to 1000 nm and (b) individual MAPbBr-100 particles indicated by red numbers with particle sizes from 750 nm to 1760 nm, scale bar $\approx 2 \ \mu m$. (c) Emission spectra of single particles derived from confocal fluorescence images of MAPBr-110 in blue symbols and MAPBr-100 in red symbols with the Gaussian fit of the highlighted particles in (a) and (b) with similar sizes 1 (blue) and 3 (red), respectively. A blue-shift of approximately 5-7 nm can be extracted which is in good agreement with the shift in emission maxima derived from steady state fluorescence data. Due to the resolution limit of 10 nm wavelength detection window the emission maxima are only estimations. (d) Table of emission maxima derived by a Gaussian fit in correlation to the particle size from single particle emission spectra. In the range of the particle size distribution, the effect of the size on the emission spectra in MAPBr₃ is negligible.