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Mechanism of Non-Catalytic Chemical Vapor Deposition Growth of All-Inorganic

CsPbX₃ (X=Br, Cl) Nanowires

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Fig. S1 Schematic diagram of the chemical vapor deposition (CVD) setup used for growing all-inorganic CsPbX₃ (X = Br, Cl) NWs in the non-catalytic chemical vapor deposition (NC-CVD) synthesis.



Fig. S2 Dark field (DF) optical microscopy images showing self-assembly of the all-inorganic CsPbBr₃ particles in growing CsPbBr₃ nanowires (NWs) in the non-catalytic chemical vapor deposition (NC-CVD) synthesis. NWs' growth on (a-e) SiO₂/Si and (f-g) c-Al₂O₃ substrates. Scale bar is 20 μ m.



Fig. S3 A schematic illustration of the steps involved in the self-assembly mechanism in the non-catalytic chemical vapor deposition (NC-CVD) synthesis of all-inorganic CsPbX₃ (Br, Cl) nanowires.



Fig. S4 Morphology and Microstructural analysis. (a) Field emission scanning electron microscopy (FESEM) image of CsPbCl₃ NWs grown on c-Al₂O_{3.} (b) HRTEM image and (c) X-ray diffraction spectra of CsPbCl₃ NWs grown on c-Al₂O₃.



Fig. S5 High resolution X-ray photoelectron spectroscopy (XPS). (a) Calibration spectrum of C 1s. The core level spectra of (b) Cs $3d_{5/2}$; (c) Pb $4f_{7/2}$ and Pb $4f_{5/2}$; and (d) Br $3d_{3/2}$ obtained from a self-assembled CsPbBr₃ perovskite nanowire grown by the non-catalytic chemical vapor deposition (NC-CVD) process.



Fig. S6 Energy dispersive X-ray spectroscopy (EDS) maps showing the distribution of various elements in CsPbX₃ (X = Br, Cl) NWs. These elemental maps were taken in a TEM (a) A dark field image of CsPbBr₃ structures drop casted on C coated Cu grid and corresponding elements maps (b) A TEM image of CsPbCl₃ structures drop casted on C coated Cu grid and the corresponding elements maps.

Here, it is important to mention that the NWs were found to be very sticky on the Al₂O₃ substrates and was very difficult to transfer a complete NW structure. Therefore, EDS studies were performed on the structures available on the copper (Cu) grid obtained from the drop casting of the sonicated extracts of the self-assembled CsPbBr₃ and CsPbCl₃ NWs grown on sapphire followed by a hot plate drying.



Fig. S7 Room temperature absorbance and photoluminescence spectra of CsPbBr₃ NWs grown on c-Al₂O₃. The close proximity of the absorption edge and the PL peak indicates that the PL emission corresponds to the band edge emission of the self-assembled CsPbBr₃ NWs.



Fig. S8 Confocal micro-Raman characterization of various morphological features of selfassembled CsPbBr₃ halide perovskites. (a) Low resolution camera images of the studied CsPbBr₃ structures including complete nanowires, dots and incomplete nanowires; (b) the corresponding Raman spectra. No spectral shift is observed for the various structures under investigations showing their crystalline homogeneity.



Fig. S9 Fluorescence microscopy images obtained from a Nikon ECLIPSE TS 100. (a-i) Different stages of self-assembly process of the CsPbBr₃ nanowire formation. Nanowires are grown on c-plane sapphire by non-catalytic chemical vapor deposition (NC-CVD) method. Same fluorescence from CsPbBr₃ dot like spherical halide particles, incomplete/ fragmented

nanowires and complete nanowires resembles the same material composition in all different nanoscale features. Difference in the fluorescence intensity may arise from the size and thickness of the structures. Scale bar (a-c) 50 μ m and (d-i) 10 μ m.

Verification of Surface Guiding or Graphoepitaxial Effect of c-Al₂O₃ on Halide NWs Growth

Surface guiding and graphoepitaxial effects have been reported for the vapor growth of IHP NWs on sapphire substrates.¹⁻³ Following the faceted growth of CsPbCl₃ and CsPbBr₃ NWs on c-Al₂O₃, we performed a systematic study to see if there is any surface guiding or graphoepitaxial effect of the sapphire substrate on the faceted growth of the halide nanowires. Two pieces of cleaned sapphire substrates were annealed at the same CVD growth environment maintaining the same maximum growth time (60 mins) and temperature (500°C), similar to those for halide nanowires growth. AFM measurement was performed on the sapphire substrates just before and after annealing. No morphological change with any nanogroove was noticed on the substrates. This confirms that there was no guiding or graphoepitaxial effect on growing the NWs on c-Al₂O₃ substrate. The self-induced assembly of the halide particles was, therefore, taken place following the inherent hexagonal crystal facets of the c-Al₂O₃ substrate.



Fig. S10 AFM measurements of clean-bare sapphire substrate- (a) before annealing and (b) after annealing. Annealing was performed using the same time (60 min) and temperature (500°C) as that of the NC-CVD growth of CsPbX₃ NWs.

References

- E. Oksenberg, E. Sanders, R. Popovitz-Biro, L. Houben and E. Joselevich, *Nano Lett.*, 2018, 18, 424–433.
- M. Shoaib, X. Wang, X. Zhang, X. Wang, H. Zhou, T. Xu, X. Hu, H. Liu, X. Fan, W.
 Zheng, T. Yang, S. Yang, Q. Zhang, X. Zhu, L. Sun and A. Pan, *J. Am. Chem. Soc.*,
 2017, 139, 15592–15595.
- X. Wang, M. Shoaib, X. Wang, X. Zhang, M. He, Z. Luo, W. Zheng, H. Li, T. Yang,
 X. Zhu, L. Ma and A. Pan, *ACS Nano*, 2018, **12**, 6170–6178.