Monocrystalline halide perovskite nanostructures for optoelectronic applications

Khoram, P.

Citation for published version (APA):
Khoram, P. (2018). Monocrystalline halide perovskite nanostructures for optoelectronic applications.
References

[1] https://www.mindat.org.
[2] F. Galasso, STRUCTURE OF PEROVSKITE-TYPE COMPOUNDS, in Structure, Properties and Preparation of Perovskite-Type Compounds, pages 3–49, Elsevier, 1969.
[3] J. Alberio, A. R. Malik, and H. Garcia, Influence of the Composition of Hybrid Perovskites on their Performance in Solar Cells, J. Mater. Chem. A (2016).
[4] S. Brittman, G. W. P. Adhyaksa, and E. C. Garnett, The expanding world of hybrid perovskites: materials properties and emerging applications, MRS Communications, 1 (2015).
[5] V. M. Goldschmidt, Die Gesetze der Krystallochemie, Naturwissenschaften 14, 477 (1926).
[6] D. M. Giaquinta and H.-C. zur Loye, Structural Predictions in the ABO3 Phase Diagram, Chemistry of Materials 6, 365 (1994).
[7] C. Li, K. C. K. Soh, and P. Wu, Formability of ABO3 perovskites, Journal of Alloys and Compounds 372, 40 (2004).
[8] J. Zhu, H. Li, L. Zhong, P. Xiao, X. Xu, X. Yang, Z. Zhao, and J. Li, Perovskite oxides: Preparation, characterizations, and applications in heterogeneous catalysis, ACS Catalysis 4, 2917 (2014).
[9] H. L. Wells, Über die Cäsium- und Kalium-Bleihalogenide, Zeitschrift für anorganische Chemie 3, 195 (1893).
[10] C. Li, X. Lu, W. Ding, L. Feng, Y. Gao, and Z. Guo, Formability of ABX 3 (X = F, Cl, Br, I) halide perovskites, Acta Crystallographica Section B Structural Science 64, 702 (2008).
[11] D. Weber, (CH3NH3PbX3), a Pb(II)-System with Cubic Perovskite Structure, Zeitschrift für Naturforschung B 33b, 1443 (1978).
[12] D. Weber, CH3NH3SnBrxI3-x (x=0-3), a Sn(II)-system with the cubic perovskite structure, Zeitschrift für Naturforschung 33b, 862 (1978).
[13] M. a. Green, A. Ho-Baillie, and H. J. Snaith, The emergence of perovskite solar cells, Nature Photonics 8, 506 (2014).
[14] C. C. Stoumpos and M. G. Kanatzidis, The Renaissance of Halide Perovskites and Their Evolution as Emerging Semiconductors, Accounts of Chemical Research (2015).
[15] D. B. Mitzi, C. A. Feild, W. T. A. Harrison, and A. M. Guloy, Conducting Tin Halides with a Layered Organic-based Perovskite Structure, Nature 369, 467 (1994).
[16] D. B. Mitzi, C. Feild, Z. Schlesinger, and R. B. Laibowitz, Transport, Optical, and Magnetic Properties of the Conducting Halide Perovskite CH3NH3SnI3, Journal of Solid State Chemistry 114, 159 (1995).
[17] D. B. Mitzi, S. Wang, C. a. Feild, C. a. Chess, and a. M. Guloy, "Conducting Layered Organic-inorganic Halides Containing <110>-Oriented Perovskite Sheets," Science (New York, N.Y.) 267, 1473 (1995).

[18] D. B. Mitzi, K. Chondroudis, and C. R. Kagan, "Design, Structure, and Optical Properties of Organic-inorganic Perovskites Containing an Oligothiophene Chromophore," Inorganic Chemistry 38, 6246 (1999).

[19] A. Kojima, K. Teshima, Y. Shirai, and T. Miyasaka, "Organometal Halide Perovskites as Visible-light Sensitizers for Photovoltaic Cells," Journal of the American Chemical Society 131, 6050 (2009).

[20] https://www.nrel.gov/pv/assets/images/efficiency-chart.png.

[21] M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami, and H. J. Snaith, "Efficient Hybrid Solar Cells Based on Meso-superstructured Organometal Halide Perovskites," Science 338, 643 (2012).

[22] M. Liu, M. B. Johnston, and H. J. Snaith, "Efficient planar heterojunction perovskite solar cells by vapour deposition," Nature 501, 395 (2013).

[23] H. J. Snaith, "Perovskites: The Emergence of a New Era for Low-Cost, High-Efficiency Solar Cells," The Journal of Physical Chemistry Letters 4, 3623 (2013).

[24] N. J. Jeon, J. H. Noh, W. S. Yang, Y. C. Kim, S. Ryu, J. Seo, and S. I. Seok, "Compositional engineering of perovskite materials for high-performance solar cells," Nature 517, 476 (2015).

[25] W. Nie, H. Tsai, R. Asadpour, J.-C. Blancon, A. J. Neukirch, G. Gupta, J. J. Crochet, M. Chhowalla, S. Tretiak, M. A. Alam, H.-L. Wang, and A. D. Mohite, "High-efficiency solution-processed perovskite solar cells with millimeter-scale grains," Science 347, 522 (2015).

[26] P. Docampo and T. Bein, "A Long-Term View on Perovskite Optoelectronics," Accounts of Chemical Research 49, 339 (2016).

[27] J. You, L. Meng, Z. Hong, G. Li, and Y. Yang, "Inverted planar structure of perovskite solar cells," Organic-Inorganic Halide Perovskite Photovoltaics: From Fundamentals to Device Architectures, 307 (2016).

[28] J. M. Frost, K. T. Butler, F. Brivio, C. H. Hendon, M. van Schilfgaarde, and A. Walsh, "Atomic Origins of High-Performance in Hybrid Halide Perovskite Solar Cells," Nano Letters 14, 2584 (2014).

[29] A. Miyata, A. Mitioglu, P. Plochocka, O. Portugall, J. T.-W. Wang, S. D. Stranks, H. J. Snaith, and R. J. Nicholas, "Direct measurement of the exciton binding energy and effective masses for charge carriers in organic–inorganic tri-halide perovskites," Nature Physics 11, 582 (2015).

[30] A. R. Srimath Kandada and A. Petrozza, "Optophysics of Hybrid Lead Halide Perovskites: The Role of Microstructure," Accounts of Chemical Research 49, 536 (2016).

[31] M. B. Johnston and L. M. Herz, "Hybrid Perovskites for Photovoltaics: Charge-Carrier Recombination, Diffusion, and Radiative Efficiencies," Accounts of Chemical Research 49, 146 (2016).

[32] J. M. Frost and A. Walsh, "What Is Moving in Hybrid Halide Perovskite Solar Cells?", Accounts of chemical research 49, 528 (2016).

[33] S. S. Zumdahl, Chemical Principles, 2005.

[34] A. West, Solid State Chemistry and its Applications, 2nd Edition, Student Edition, 2014.

[35] T. Umebayashi, K. Asai, T. Kondo, and A. Nakao, "Electronic structures of lead iodide based low-dimensional crystals," Physical Review B 67, 155405 (2003).

[36] Y. H. Chang, C. H. Park, and K. Matsuishi, First-principles study of the structural
and the electronic properties of the lead-halide-based inorganic-organic perovskites (CH3NH3)PbX3 and CsPbX3 (X = Cl, Br, I), Journal of the Korean Physical Society **44**, 889 (2004).

[37] E. Mosconi, A. Amat, M. K. Nazeeruddin, M. Grätzel, and F. De Angelis, *First-Principles Modeling of Mixed Halide Organometal Perovskites for Photovoltaic Applications*, The Journal of Physical Chemistry C **117**, 13902 (2013).

[38] T. Baikie, Y. Fang, J. M. Kadro, M. Schreyer, F. Wei, S. G. Mhaisalkar, M. Graetzel, and T. J. White, *Synthesis and crystal chemistry of the hybrid perovskite (CH3NH3)PbI3 for solid-state sensitised solar cell applications*, Journal of Materials Chemistry A **1**, 5628 (2013).

[39] M. R. Filip, G. E. Eperon, H. J. Snaith, and F. Giustino, *Steric engineering of metal-halide perovskites with tunable optical band gaps*, Nature Communications **5**, 5757 (2014).

[40] B. R. Sutherland and E. H. Sargent, *Perovskite photonic sources*, Nature Photonics **10**, 295 (2016).

[41] M. Wei, Y.-H. Chung, Y. Xiao, and Z. Chen, *Color tunable halide perovskite CH3NH3PbBr3xClx emission via annealing*, Organic Electronics **26**, 260 (2015).

[42] Y. Wang, X. Sun, R. Shivanna, Y. Yang, Z. Chen, Y. Guo, G.-C. Wang, E. Wertz, F. Deschler, Z. Cai, H. Zhou, T.-M. Lu, and J. Shi, *Photon Transport in One-Dimensional Incommensurately Epitaxial CsPbX3 3 Arrays*, Nano Letters, acs.nanolett.6b04297 (2016).

[43] G. Xing, N. Mathews, S. S. Lim, N. Yantara, X. Liu, D. Sabha, M. Grätzel, S. Mhaisalkar, and T. C. Sum, *Low-temperature solution-processed wavelength-tunable perovskites for lasing*, Nature Materials **13**, 476 (2014).

[44] C. M. Sutter-Fella, Y. Li, M. Amani, J. W. Ager, F. M. Toma, E. Yablonovitch, I. D. Sharp, and A. Javey, *High Photoluminescence Quantum Yield in Band Gap Tunable Bromide Containing Mixed Halide Perovskites*, Nano Letters **16**, 800 (2016).

[45] J. Xing, X. F. Liu, Q. Zhang, S. T. Ha, Y. W. Yuan, C. Shen, T. C. Sum, and Q. Xiong, *Vapor Phase Synthesis of Organometal Halide Perovskite Nanowires for Tunable Room-Temperature Nanolasers*, Nano Letters **15**, 4571 (2015).

[46] F. Zhang, H. Zhong, C. Chen, X.-G. Wu, X. Hu, H. Huang, J. Han, B. Zou, and Y. Dong, *Brightly Luminescent and Color-Tunable Colloidal CH3NH3PbX3 (X = Br, I, Cl) Quantum Dots: Potential Alternatives for Display Technology*, ACS nano (2015).

[47] S. a. Kulkarni, T. Baikie, P. P. Boix, N. Yantara, N. Mathews, and S. Mhaisalkar, *Bandgap tuning of lead halide perovskites using a sequential deposition process*, Journal of Materials Chemistry A **2**, 9221 (2014).

[48] N. K. Kumawat, A. Dey, A. Kumar, S. P. Gopinathan, K. L. Narasimhan, and D. Kabra, *Band Gap Tuning of CH3NH3Pb(1-x)Brx(Cl-x)3 Hybrid Perovskite for Blue Electroluminescence*, ACS Applied Materials and Interfaces **7**, 13119 (2015).

[49] R. J. Sutton, G. E. Eperon, L. Miranda, E. S. Parrott, B. A. Kamino, J. B. Patel, M. T. Hörantner, M. B. Johnston, A. A. Haghighirad, D. T. Moore, and H. J. Snaith, *Bandgap-Tunable Cesium Lead Halide Perovskites with High Thermal Stability for Efficient Solar Cells*, Advanced Energy Materials, n/a (2016).

[50] Y. Tong, E. Bladt, M. F. Aygüler, A. Manzi, K. Z. Milowska, V. A. Hintermayr, P. Docampo, S. Bals, A. S. Urban, L. Polavarapu, and J. Feldmann, *Highly Luminescent Cesium Lead Halide Perovskite Nanocrystals with Tunable Composition and Thickness by Ultrasonication*, Angewandte Chemie International Edition (2016).

[51] Q. A. Akkerman, V. D’Innocenzo, S. Accornero, A. Scarpellini, A. Petrozza, M. Prato, and L. Manna, *Tuning the optical properties of cesium lead halide perovskite nanocrystals*
by anion exchange reactions, Journal of the American Chemical Society 137, 10276 (2015).

[52] K. Yamada, K. Nakada, Y. Takeuchi, K. Nawa, and Y. Yamane, Tunable Perovskite Semiconductor CH3NH3SnX3 (X: Cl, Br, or I) Characterized by X-ray and DTA, Bulletin of the Chemical Society of Japan 84, 926 (2011).

[53] H.-J. Feng, T. R. Paudel, E. Y. Tsymbal, and X. C. Zeng, Tunable optical properties and charge separation in CH3NH3SnxPb1-xI3/TiO2 based planar perovskites cells., Journal of the American Chemical Society (2015).

[54] G. E. Eperon, S. D. Stranks, C. Menelaou, M. B. Johnston, L. M. Herz, and H. J. Snaith, Formamidinium lead trihalide: a broadly tunable perovskite for efficient planar heterojunction solar cells, Energy & Environmental Science 7, 982 (2014).

[55] F. Hao, C. C. Stoumpos, R. P. H. Chang, and M. G. Kanatzidis, Anomalous band gap behavior in mixed Sn and Pb perovskites enables broadening of absorption spectrum in solar cells Anomalous band gap behavior in mixed Sn and Pb perovskites enables broadening of absorption spectrum in solar cells, Journal of the American Chemical Society 136, 8094 (2014).

[56] L. Lang, J.-H. Yang, H.-R. Liu, H. Xiang, and X. Gong, First-principles study on the electronic and optical properties of cubic ABX3 halide perovskites, Physics Letters A 378, 290 (2014).

[57] A. Amat, E. Mosconi, E. Ronca, C. Quarti, P. Umari, M. K. Nazeeruddin, M. Grätzel, and F. De Angelis, Cation-induced band-gap tuning in organohalide perovskites: Interplay of spin-orbit coupling and octahedra tilting, Nano Letters 14, 3608 (2014).

[58] W.-J. Yin, T. Shi, and Y. Yan, Unusual defect physics in CH3NH3PbI3 perovskite solar cell absorber, Applied Physics Letters 104, 63903 (2014).

[59] K. X. Steirer, P. Schulz, G. Teeter, V. Stevanovic, M. Yang, K. Zhu, and J. J. Berry, Defect Tolerance in Methylammonium Lead Triiodide Perovskite, ACS Energy Letters 1, 360 (2016).

[60] J. Kang and L. W. Wang, High Defect Tolerance in Lead Halide Perovskite CsPbBr3, Journal of Physical Chemistry Letters 8, 489 (2017).

[61] W. Shockley and W. T. Read, Statistics of the Recombination of Holes and Electrons, Physical Review 87, 835 (1952).

[62] R. N. Hall, Electron-Hole Recombination in Germanium, Physical Review 87, 387 (1952).

[63] D. Fitzgerald and A. Grove, Surface recombination in semiconductors, Surface Science 9, 347 (1968).

[64] A. R. Beattie and P. T. Landsberg, Auger Effect in Semiconductors, Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences 249, 16 (1959).

[65] J. M. Richter, M. Abdí-Jalebi, A. Sadhanala, M. Tabachnyk, J. P. Rivett, L. M. Pazos-Outón, K. C. Gödel, M. Price, F. Deschler, and R. H. Friend, Enhancing photoluminescence yields in lead halide perovskites by photon recycling and light out-coupling, Nature Communications 7, 13941 (2016).

[66] M. Beard and R. Ellingson, Multiple exciton generation in semiconductor nanocrystals: Toward efficient solar energy conversion, Laser & Photonics Review 2, 377 (2008).

[67] L. M. Herz, Charge-Carrier Dynamics in Organic-Inorganic Metal Halide Perovskites, Annual Review of Physical Chemistry 67, 65 (2016).

[68] L. M. Herz, Charge-Carrier Mobilities in Metal Halide Perovskites: Fundamental Mechanisms and Limits, ACS Energy Letters 2, 1539 (2017).

[69] I. Pelant and J. Valenta, Luminescence Spectroscopy of Semiconductors, volume
REFERENCES
9780199588, 2012.
[70] C. S. Ponseca, Y. Tian, V. Sundström, and I. G. Scheblykin, Excited state and charge-carrier dynamics in perovskite solar cell materials, Nanotechnology **27**, 82001 (2016).
[71] G. W. P. Adhyaksa, S. Brittmann, . Haralds, A. Lof, X. Li, T. Duevski, D. P. Fenning, and E. C. Garnett, Understanding detrimental and beneficial grain boundary effects in halide perovskites.
[72] M. B. Johnston and L. M. Herz, Hybrid Perovskites for Photovoltaics: Charge-Carrier Recombination, Diffusion, and Radiative Efficiencies, Accounts of Chemical Research **49**, 146 (2016).
[73] X. Wu, M. T. Trinh, D. Niesner, H. Zhu, Z. Norman, J. S. Owen, O. Yaffe, B. J. Kudisch, and X. Zhu, Trap States in Lead Iodide Perovskites, Journal of the American Chemical Society **137**, 2089 (2015).
[74] J. M. Ball and A. Petrozza, Defects in perovskite-halides and their effects in solar cells, Nature Energy **1**, 16149 (2016).
[75] V. Adinolfi, M. Yuan, E. S. Thibau, D. Shi, M. I. Saidaminov, P. Kanjanaboos, D. Kopilovic, S. Hoogland, Z. H. Lu, O. M. Bakr, and E. H. Sargent, The In-Gap Electronic State Spectrum of Methylammonium Lead Iodide Single-Crystal Perovskites, Advanced Materials **28**, 3406 (2016).
[76] D. Shi, V. Adinolfi, R. Comin, M. Yuan, E. Alarousu, A. Buin, Y. Chen, S. Hoogland, A. Rothenberger, K. Katsiev, Y. Losovyj, X. Zhang, P. A. Dowben, O. F. Mohammed, E. H. Sargent, and O. M. Bakr, Low trap-state density and long carrier diffusion in organolead trihalide perovskite single crystals, Science **347**, 519 (2015).
[77] A. Buin, P. Pietsch, O. Voznyy, R. Comin, A. H. Ip, E. H. Sargent, and B. Xu, Materials Processing Routes to Trap-free Halide Perovskites, Nano letters **14**, 6281 (2014).
[78] U. Rau, Reciprocity relation between photovoltaic quantum efficiency and electroluminescent emission of solar cells, Physical Review B - Condensed Matter and Materials Physics **76**, 1 (2007).
[79] J. F. Geisz, M. A. Steiner, I. García, S. R. Kurtz, and D. J. Friedman, Enhanced external radiative efficiency for 20.8% efficient single-junction GaInP solar cells, Applied Physics Letters **103**, 041118 (2013).
[80] F. Deschler, M. Price, S. Pathak, L. Klintberg, D. D. Jarausch, R. Higler, S. Huettner, T. Leijtens, S. D. Stranks, H. J. Snaith, M. Atature, R. T. Phillips, and R. H. Friend, High Photoluminescence Efficiency and Optically-Pumped Lasing in Solution-Processed Mixed Halide Perovskite Semiconductors, The Journal of Physical Chemistry Letters **5**, 1421 (2014).
[81] J. S. Manser and P. V. Kamat, Band filling with free charge carriers in organometal halide perovskites, Nature Photonics **8**, 737 (2014).
[82] M. Sheik-Bahae and R. I. Epstein, Can Laser Light Cool Semiconductors?, Physical Review Letters **92**, 247403 (2004).
[83] N.-G. Park, M. Grätzel, and T. Miyasaka, editors, Organic-Inorganic Halide Perovskite Photovoltaics, Springer International Publishing, Cham, 2016.
[84] W. Zhang, G. E. Eperon, and H. J. Snaith, Metal halide perovskites for energy applications, Nature Energy **1**, 16048 (2016).
[85] S. Adjokatse, H. H. Fang, and M. A. Loi, Broadly tunable metal halide perovskites for solid-state light-emission applications, Materials Today **20**, 413 (2017).
[86] Y.-H. Kim, H. Cho, and T.-W. Lee, Metal halide perovskite light emitters, Proceedings of the National Academy of Sciences **113**, 11694 (2016).
[87] H. Wang and D. H. Kim, Perovskite-based photodetectors: materials and devices, Chem.
REFERENCES

Soc. Rev. 46, 5204 (2017).
[88] M. Ahmadi, T. Wu, and B. Hu, A Review on Organic–Inorganic Halide Perovskite Photodetectors: Device Engineering and Fundamental Physics, Advanced Materials 29, 1 (2017).
[89] J.-H. Im, C.-R. Lee, J.-W. Lee, S.-W. Park, and N.-G. Park, 6.5% Efficient Perovskite Quantum-Dot-Sensitized Solar Cell, Nanoscale 3, 4088 (2011).
[90] H.-S. Kim, C.-R. Lee, J.-H. Im, K.-B. Lee, T. Moehl, A. Marchioro, S.-J. Moon, R. Humphry-Baker, J.-H. Yum, J. E. Moser, M. Grätzel, and N.-G. Park, Lead Iodide Perovskite Sensitized All-Solid-State Submicron Thin Film Mesoscopic Solar Cell with Efficiency Exceeding 9%, Scientific Reports 2, 591 (2012).
[91] J. M. Ball, M. M. Lee, A. Hey, and H. J. Snaith, Low-temperature processed meso-superstructured to thin-film perovskite solar cells, Energy & Environmental Science 6, 1739 (2013).
[92] S. D. Stranks, G. E. Eperon, G. Grancini, C. Menelaou, M. J. P. Alcocer, T. Leijtens, L. M. Herz, A. Petrozza, and H. J. Snaith, Electron-hole diffusion lengths exceeding 1 micrometer in an organometal trihalide perovskite absorber, Science (New York, N.Y.) 342, 341 (2013).
[93] M. A. Green, Silicon Solar Cells: Advanced Principles & Practice, Centre for Photovoltaic Devices and Systems, University of New South Wales, 1995.
[94] J. Mizusaki, K. Arai, and K. Fueki, Ionic conduction of the perovskite-type halides, Solid State Ionics 11, 203 (1983).
[95] T. Ishihara, H. Matsuda, and Y. Takita, Doped LaGaO3 Perovskite Type Oxide as a New Oxide Ionic Conductor, Journal of the American Chemical Society 116, 3801 (1994).
[96] K. Domanski, B. Roose, T. Matsui, M. Saliba, S.-H. Turren-Cruz, J.-P. Correa-Baena, C. R. Carmona, G. Richardson, J. M. Foster, F. De Angelis, J. M. Ball, A. Petrozza, N. Mine, M. K. Nazaruddin, W. Tress, M. Gratzel, U. Steiner, A. Hagfeldt, and A. Abate, Migration of cations induces reversible performance losses over day/night cycling in perovskite solar cells, Energy Environ. Sci. 10, 604 (2017).
[97] S. Van Reenen, M. Kemerink, and H. J. Snaith, Modeling Anomalous Hysteresis in Perovskite Solar Cells, Journal of Physical Chemistry Letters 6, 3808 (2015).
[98] H. J. Snaith, A. Abate, J. M. Ball, G. E. Eperon, T. Leijtens, N. K. Noel, S. D. Stranks, J. T. Wang, K. Wojciechowski, and W. Zhang, Anomalous hysteresis in perovskite solar cells, Journal of Physical Chemistry Letters 5, 1511 (2014).
[99] J. M. Frost, K. T. Butler, and A. Walsh, Molecular ferroelectric contributions to anomalous hysteresis in hybrid perovskite solar cells, APL Materials 2, 081506 (2014).
[100] C. Quarti, E. Mosconi, and F. De Angelis, Interplay of orientational order and electronic structure in methylammonium lead iodide: Implications for solar cell operation, Chemistry of Materials 26, 6557 (2014).
[101] K. Domanski, J. P. Correa-Baena, N. Mine, M. K. Nazaruddin, A. Abate, M. Saliba, W. Tress, A. Hagfeldt, and M. Graetzel, Not All That Glitters Is Gold: Metal-Migration-Induced Degradation in Perovskite Solar Cells, ACS Nano 10, 6306 (2016).
[102] W. Nie, J.-C. Blanccon, A. J. Neukirch, K. Appavoo, H. Tsai, M. Chhowalla, M. A. Alam, M. Y. Sfeir, C. Katan, J. Even, S. Tretiak, J. J. Crochet, G. Gupta, and A. D. Mohite, Light-activated photocurrent degradation and self-healing in perovskite solar cells, Nature Communications 7, 11574 (2016).
[103] W. Tress, Metal Halide Perovskites as Mixed Electronic-Ionic Conductors: Challenges and Opportunities-From Hysteresis to Memristivity, The Journal of Physical Chemistry Letters 8, 3106 (2017).
REFERENCES

[104] J.-H. Choy, S.-H. Jeong, M.-H. Park, Y.-H. Kim, C. Wolf, C.-L. Lee, J. H. Heo, A. Sadhanala, N. Myoung, S. Yoo, S. H. Im, R. H. Friend, and T.-W. Lee, Overcoming the electroluminescence efficiency limitations of perovskite light-emitting diodes, Science 350, 1222 (2015).

[105] X. Y. Chin, D. Corteccia, J. Yin, A. Bruno, and C. Soci, Lead Iodide Perovskite Light-Emitting Field-Effect Transistor, Arxiv 6, Advance (2015).

[106] W. Shockley and H. J. Queisser, Detailed Balance Limit of Efficiency of p-n Junction Solar Cells, Journal of Applied Physics 32, 510 (1961).

[107] A. Sadhanala, S. Ahmad, B. Zhao, N. Giesbrecht, P. Pearce, F. Deschler, R. L. Hoye, K. C. Goedel, T. Bein, P. Docampo, S. E. Dutton, M. De Volder, and R. H. Friend, Blue-Green Colour Tunable Solution Processable Organolead Chloride-Bromide Mixed Halide Perovskites for Optoelectronic Applications, Nano Letters, 150803110321002 (2015).

[108] S. D. Stranks and H. J. Snaith, Metal-halide perovskites for photovoltaic and light-emitting devices, Nature Nanotechnology 10, 391 (2015).

[109] S. A. Veldhuis, P. P. Boix, N. Yantara, M. Li, T. C. Sum, N. Mathews, and S. G. Mhaisalkar, Perovskite Materials for Light-Emitting Diodes and Lasers, Advanced Materials, 6804 (2016).

[110] X. Hong, T. Ishihara, and A. Nurminko, Photoconductivity and electroluminescence in lead iodide based natural quantum well structures, Solid State Communications 84, 657 (1992).

[111] M. Era, S. Morimoto, T. Tsutsumi, and S. Saito, Organic-inorganic heterostructure electroluminescent device using a layered perovskite semiconductor, Applied Physics Letters 65, 676 (1994).

[112] T. Hattori, T. Taira, M. Era, T. Tsutsui, and S. Saito, Highly efficient electroluminescence from a heterostructure device combined with emissive layered-perovskite and an electron-transporting organic compound, Chemical Physics Letters 254, 103 (1996).

[113] A. Kojima, M. Iekami, K. Teshima, and T. Miyasaka, Highly Luminescent Lead Bromide Perovskite Nanoparticles Synthesized with Porous Alumina Media, Chemistry Letters 41, 397 (2012).

[114] Z.-K. Tan, R. S. Moghaddam, M. L. Lai, P. Docampo, R. Higler, F. Deschler, M. Price, A. Sadhanala, L. M. Pazos, D. Credgington, F. Hanusch, T. Bein, H. J. Snaith, and R. H. Friend, Bright light-emitting diodes based on organometal halide perovskite, Nature Nanotechnology 9, 1 (2014).

[115] S. Pathak, N. Sakai, F. Wisnivesky Rocca Rivarola, S. D. Stranks, J. Liu, G. Eperon, C. Ducati, K. Wojciechowski, J. T. Griffiths, A. A. Haghighirad, A. Pellarque, R. H. Friend, and H. J. Snaith, Perovskite Crystals for Tuneable White Light Emission, Chemistry of Materials, acs.chemmater.5b03769 (2015).

[116] H. Huang, H. Lin, S. V. Kershaw, A. S. Susha, W. C. H. Choy, and A. L. Rogach, Polyhedral Oligomeric Silsesquioxane Enhances the Brightness of Perovskite Nanocrystal-Based Green Light-Emitting Devices, The Journal of Physical Chemistry Letters 7, 4398 (2016).

[117] J. Wang, N. Wang, Y. Jin, J. Si, Z.-K. Tan, H. Du, L. Cheng, X. Dai, S. Bai, H. He, Z. Ye, M. L. Lai, R. H. Friend, and W. Huang, Interfacial Control Toward Efficient and Low-Voltage Perovskite Light-Emitting Diodes, Advanced Materials 27, 2311 (2015).

[118] Y.-H. Kim, H. Cho, J. H. Heo, T.-S. Kim, N. Myoung, C.-L. Lee, S. H. Im, and T.-W. Lee, Multicolored Organic/Inorganic Hybrid Perovskite Light-Emitting Diodes, Advanced Materials 27, 1248 (2015).

[119] R. L. Z. Hoye, M. R. Chua, K. P. Musselman, G. Li, M.-L. Lai, Z.-K. Tan, N. C. Greenham,
REFERENCES

J. L. MacManus-Driscoll, R. H. Friend, and D. Credgington, *Enhanced Performance in Fluorene-Free Organometal Halide Perovskite Light-Emitting Diodes using Tunable, Low Electron Affinity Oxide Electron Injectors*, Advanced Materials **27**, 1414 (2015).

[120] J. C. Yu, D. B. Kim, G. Baek, B. R. Lee, E. D. Jung, S. Lee, J. H. Chu, D.-K. Lee, K. J. Choi, S. Cho, and M. H. Song, *High-Performance Planar Perovskite Optoelectronic Devices: A Morphological and Interfacial Control by Polar Solvent Treatment*, Advanced Materials, n/a (2015).

[121] Z.-F. Shi, X.-G. Sun, D. Wu, T.-T. Xu, S.-W. Zhuang, Y.-T. Tian, X.-J. Li, and G.-T. Du, *High-performance planar green light-emitting diodes based on a PEDOT:PSS/CH$_3$NH$_3$PbBr$_3$/ZnO sandwich structure*, Nanoscale **8**, 10035 (2016).

[122] J. C. Yu, D. B. Kim, E. D. Jung, B. R. Lee, and M. H. Song, *High-performance perovskite light-emitting diodes via morphological control of perovskite films*, Nanoscale **8**, 7036 (2016).

[123] H. Zhu, Y. Fu, F. Meng, X. Wu, Z. Gong, Q. Ding, M. V. Gustafsson, M. T. Trinh, S. Jin, and X.-Y. Zhu, *Lead halide perovskite nanowire lasers with low lasing thresholds and high quality factors*, Nature Materials **14**, 636 (2015).

[124] X. Liu, L. Niu, C. Wu, C. Cong, H. Wang, Q. Zeng, H. He, Q. Fu, W. Fu, T. Yu, C. Jin, Z. Liu, and T. C. Sum, *Periodic Organic-Inorganic Halide Perovskite Microplatelet Arrays on Silicon Substrates for Room-Temperature Lasing*, Advanced Science **3**, 1600137 (2016).

[125] Q. Zhang, S. T. Ha, X. Liu, T. C. Sum, and Q. Xiong, *Room-Temperature Near-Infrared High-Q Perovskite Whispering-Gallery Planar Nanolasers*, Nano Letters **14**, 5995 (2014).

[126] D. Kang, S. R. Pae, J. Shim, G. Yoo, J. Jeon, J. W. Leem, J. S. Yu, S. Lee, B. Shin, and J. Park, *An Ultrahigh-Performance Photodetector based on a Perovskite–Transition-Metal-Dichalcogenide Hybrid Structure*, Advanced Materials (2016).

[127] W. Deng, L. Huang, X. Xu, X. Zhang, X. Jin, S.-T. Lee, and J. Jie, *Ultrahigh-Responsivity Photodetectors from Perovskite Nanowire Arrays for Sequentially Tunable Spectral Measurement*, Nano Letters **17**, 2482 (2017).

[128] L. Dou, Y. M. Yang, J. You, Z. Hong, W.-H. Chang, G. Li, and Y. Yang, *Solution-processed hybrid perovskite photodetectors with high detectivity*, Nature communications **5**, 5404 (2014).

[129] J. Yu, X. Chen, Y. Wang, H. Zhou, M. Xue, Y. Xu, Z. Li, C. Ye, J. Zhang, P. A. van Aken, P. D. Lund, and H. Wang, *A high-performance self-powered broadband photodetector based on a CH$_3$NH$_3$PbI$_3$ perovskite/ZnO nanorod array heterostructure*, Journal of Materials Chemistry C **4**, 7302 (2016).

[130] Q. Lin, A. Armin, P. L. Burn, and P. Meredith, *Filterless narrowband visible photodetectors*, Nature Photonics **9**, 687 (2015).

[131] L. Gao, K. Zeng, J. Guo, C. Ge, J. Du, Y. Zhao, C. Chen, H. Deng, Y. He, H. Song, G. Niu, and J. Tang, *Passivated Single-Crystalline CH$_3$NH$_3$PbI$_3$ Nanowire Photodetector with High Detectivity and Polarization Sensitivity*, Nano Letters **16**, 7446 (2016).

[132] Y. Fang, Q. Dong, Y. Shao, Y. Yuan, and J. Huang, *Highly narrowband perovskite single-crystal photodetectors enabled by surface-charge recombination*, Nature Photonics *advance on* (2015).

[133] S. Yakunin, M. Sytnyk, D. Kriegner, S. Shrestha, M. Richter, G. J. Matt, H. Azimi, C. J. Brabec, J. Stangl, M. V. Kovalenko, and W. Heiss, *Detection of X-ray photons by solution-processed lead halide perovskites*, Nature Photonics (2015).

[134] L. Shen, Y. Fang, D. Wang, Y. Bai, Y. Deng, M. Wang, Y. Lu, and J. Huang, *A Self-Powered, Sub-nanosecond-Response Solution-Processed Hybrid Perovskite Photodetector for
REFERENCES

Time-Resolved Photoluminescence-Lifetime Detection, Advanced Materials 28, 10794 (2016).

[135] B. R. Sutherland, A. K. Johnston, A. H. Ip, J. Xu, V. Adinolfi, P. Kanjanaboos, and E. H. Sargent, Sensitive, Fast, and Stable Perovskite Photodetectors Exploiting Interface Engineering, ACS Photonics 2, 1117 (2015).

[136] Y. Fang and J. Huang, Resolving Weak Light of Sub-picowatt per Square Centimeter by Hybrid Perovskite Photodetectors Enabled by Noise Reduction, Advanced Materials 27, 2804 (2015).

[137] Y. Lee, J. Kwon, E. Hwang, C.-H. Ra, W. J. Yoo, J.-H. Ahn, J. H. Park, and J. H. Cho, High-Performance Perovskite-Graphene Hybrid Photodetector, Advanced Materials 27, 41 (2015).

[138] J. Ding and Q. Yan, Progress in organic-inorganic hybrid halide perovskite single crystal: growth techniques and applications, Science China Materials 60, 1063 (2017).

[139] Y. Dang, D. Ju, L. Wang, and X. Tao, Recent progress in the synthesis of hybrid halide perovskite single crystals, CrystEngComm 18, 4476 (2016).

[140] Q. Dong, Y. Fang, Y. Shao, P. Mulligan, J. Qiu, L. Cao, and J. Huang, Electron-hole diffusion lengths > 175 m in solution-grown CH3NH3PbI3 single crystals, Science 347, 967 (2015).

[141] H.-H. Fang, R. Raissa, M. Abdu-Aguye, S. Adjokatse, G. R. Blake, J. Even, and M. A. Loi, Photophysics of Organic-Inorganic Hybrid Lead Iodide Perovskite Single Crystals, Advanced Functional Materials 25, n/a (2015).

[142] D. Valverde-Chavez, C. S. Ponseca, C. Stoumpos, A. Yartsev, M. Kanatzidis, V. Sundstrom, and D. G. Cooke, Intrinsic femtosecond charge generation dynamics in single crystal CH3NH3PbI3, Energy Environ. Sci. (2015).

[143] A. A. Zhumekenov, M. I. Saidaminov, M. A. Haque, E. Alarousu, S. P. Sarmah, B. Murali, I. Dursun, X.-H. Miao, A. L. Abdelhady, T. Wu, O. F. Mohammed, and O. M. Bakr, Formamidinium Lead Halide Perovskite Crystals with Unprecedented Long Carrier Dynamics and Diffusion Length, ACS Energy Letters 1, 32 (2016).

[144] Y. Yang, Y. Yan, M. Yang, S. Choi, K. Zhu, J. M. Luther, and M. C. Beard, Low surface recombination velocity in solution-grown CH3NH3PbBr3 perovskite single crystal, Nature Communications 6, 7961 (2015).

[145] Q. Lv, W. He, Z. Lian, J. Ding, Q. Li, and Q. Yan, Anisotropic moisture erosion of CH 3 NH 3 PbI 3 single crystals, CrystEngComm 19, 901 (2017).

[146] Z. Lian, Q. Yan, Q. Lv, Y. Wang, L. Liu, L. Zhang, S. Pan, Q. Li, L. Wang, and J.-L. Sun, High-Performance Planar-Type Photodetector on (100) Facet of MAPbI 3 Single Crystal, Scientific Reports 5, 16563 (2015).

[147] Y. Dang, Y. Liu, Y. Sun, D. Yuan, X. Liu, W. Lu, G. Liu, H. Xia, and X. Tao, Bulk crystal growth of hybrid perovskite material CH 3 NH 3 PbI 3, CrystEngComm 17, 665 (2015).

[148] M. I. Saidaminov, A. L. Abdelhady, G. Maculan, and O. M. Bakr, Retrograde solubility of formamidinium and methylammonium lead halide perovskites enabling rapid single crystal growth, Chemical Communications 51, 17658 (2015).

[149] M. I. Saidaminov, A. L. Abdelhady, B. Murali, E. Alarousu, V. M. Burlakov, W. Peng, I. Dursun, L. Wang, Y. He, G. Maculan, A. Goriely, T. Wu, O. F. Mohammed, and O. M. Bakr, High-quality bulk hybrid perovskite single crystals within minutes by inverse temperature crystallization, Nature Communications 6, 7586 (2015).

[150] G. Maculan, A. D. Sheik, A. L. Abdelhady, M. I. Saidaminov, M. A. Haque, B. Murali, E. Alarousu, O. F. Mohammed, T. Wu, and O. M. Bakr, CH 3 NH 3 PbCl 3 Single Crystals: Inverse Temperature Crystallization and Visible-Blind UV-Photodetector, The Journal
REFERENCES

of Physical Chemistry Letters 6, 3781 (2015).

[151] Q. Han, S.-H. Bae, P. Sun, Y.-T. Hsieh, Y. M. Yang, Y. S. Rim, H. Zhao, Q. Chen, W. Shi, G. Li, and Y. Yang, Single Crystal Formamidinium Lead Iodide (FAPbI3): Insight into the Structural, Optical, and Electrical Properties, Advanced Materials, n/a (2016).

[152] D. N. Dirin, I. Cherniukh, S. Yakunin, Y. Shynkarenko, and M. V. Kovalenko, Solution-Grown CsPbBr3 Perovskite Single Crystals for Photon Detection, Chemistry of Materials 28, 8470 (2016).

[153] H. Zhou, Z. Nie, J. Yin, Y. Sun, H. Zhuo, D. Wang, D. Li, J. Dou, X. Zhang, and T. Ma, Antisolvent diffusion-induced growth, equilibrium behaviours in aqueous solution and optical properties of CH3 NH3 PbI3 single crystals for photovoltaic applications, RSC Advances 5, 85344 (2015).

[154] N. Sarukura, T. Nawata, H. Ishibashi, M. Ishii, and T. Fukuda, Czochralski Growth of Oxides and Fluorides, in Handbook of Crystal Growth, pages 131–168, Elsevier, 2015.

[155] M. Jurisch, S. Eichler, and M. Bruder, Vertical Bridgman Growth of Binary Compound Semiconductors, in Handbook of Crystal Growth, pages 331–372, Elsevier, 2015.

[156] C. C. Stoumpos, C. D. Malliakas, J. A. Peters, Z. Liu, M. Sebastian, J. Im, T. C. Chasapis, A. C. Wibowo, D. Y. Chung, A. J. Freeman, B. W. Wessels, and M. G. Kanatzidis, Crystal Growth of the Perovskite Semiconductor CsPbI3: A New Material for High-Energy Radiation Detection, Crystal Growth & Design 13, 2722 (2013).

[157] W. Peng, L. Wang, B. Murali, K.-T. Ho, A. Bera, N. Cho, C.-F. Kang, V. M. Burlakov, J. Pan, L. Sinatra, C. Ma, W. Xu, D. Shi, E. Alarousu, A. Goriely, J.-H. He, O. F. Mohammed, T. Wu, and O. M. Bakr, Solution-Grown Monocrystalline Hybrid Perovskite Films for Hole-Transporter-Free Solar Cells, Advanced Materials 28, 3383 (2016).

[158] Y. Liu, Y. Zhang, Z. Yang, D. Yang, X. Ren, L. Pang, and S. F. Liu, Thinness- and Shape-Controlled Growth for Ultrathin Single-Crystalline Perovskite Wafers for Mass Production of Superior Photoelectronic Devices, Advanced Materials 28, 9204 (2016).

[159] H.-S. Rao, W.-G. Li, B.-X. Chen, D.-B. Kuang, and C.-Y. Su, In Situ Growth of 120 cm2 CH3 NH3 PbBr3 Perovskite Crystal Film on FTO Glass for Narrowband-Photodetectors, Advanced Materials 29, 1602639 (2017).

[160] Q. Chen, C. Zhang, M. Zhu, S. Liu, M. E. Siemens, S. Gu, J. Zhu, J. Shen, X. Wu, C. Liao, J. Zhang, X. Wang, and M. Xiao, Efficient thermal conductance in organometallic perovskite CH3NH3PbI3 films, Applied Physics Letters 108, 081902 (2016).

[161] L. Lee, J. Baek, K. S. Park, Y. E. K. Lee, N. K. Shrestha, and M. M. Sung, Wafer-scale single-crystal perovskite patterned thin films based on geometrically-confined lateral crystal growth, Nature Communications 8, 1 (2017).

[162] Y. Zhang, J. Liu, Z. Wang, Y. Xue, Q. Ou, L. Polavarapu, J. Zheng, X. Qi, and Q. Bao, Synthesis, properties, and optical applications of low-dimensional perovskites, Chem. Commun. 52, 13637 (2016).

[163] L. C. Schmidt, A. Pertegás, S. González-Carrero, O. Malinkiewicz, S. Agouram, G. Mínguez Espallargas, H. J. Bolink, R. E. Galian, and J. Pérez-Prieto, Nontemplate synthesis of CH3NH3PbBr3 perovskite nanoparticles, Journal of the American Chemical Society 136, 850 (2014).

[164] S. Gonzalez-Carrero, R. E. Galian, and J. Pérez-Prieto, Maximizing the emissive properties of CH3 NH3 PbBr3 perovskite nanoparticles, Journal of Materials Chemistry A 3, 9187 (2015).

[165] Y. Hassan, Y. Song, R. D. Pensack, A. I. Abdelrahman, Y. Kobayashi, M. A. Winnik, and G. D. Scholes, Structure-Tuned Lead Halide Perovskite Nanocrystals, Advanced Materials 28, 566 (2016).
REFERENCES

[166] S. Sun, D. Yuan, Y. Xu, A. Wang, and Z. Deng, *Ligand-Mediated Synthesis of Shape-Controlled Cesium Lead Halide Perovskite Nanocrystals via Reprecipitation Process at Room Temperature*, ACS Nano 10, 3648 (2016).

[167] M. Spina, E. Bonvin, A. Sienkiewicz, B. Náfrádi, L. Forró, and E. Horváth, *Controlled growth of CH3NH3PbI3 nanowires in arrays of open nanofluidic channels*, Scientific Reports 6, 19834 (2016).

[168] E. Horváth, M. Spina, Z. Szekrényes, K. Kamarás, R. Gaal, D. Gachet, and L. Forró, *Nanowires of Methylammonium Lead Iodide (CH 3 NH 3 PbI 3 ) Prepared by Low Temperature Solution-Mediated Crystallization*, Nano Letters 14, 6761 (2014).

[169] Q. Hu, H. Wu, J. Sun, D. Yan, Y. Gao, and J. Yang, *Large-area perovskite nanowire arrays fabricated by large-scale roll-to-roll micro-gravure printing and doctor blading*, Nanoscale 8, 5350 (2016).

[170] J.-H. Im, J. Luo, M. Franckevičius, N. Pellet, P. Gao, T. Moehl, S. M. Zakeeruddin, M. K. Nazeeruddin, M. Grätzel, and N.-G. Park, *Nanowire Perovskite Solar Cell*, Nano Letters 15, 2120 (2015).

[171] A. B. Wong, M. Lai, S. W. Eaton, Y. Yu, E. Lin, L. Dou, A. Fu, and P. Yang, *Growth and Anion Exchange Conversion of CH 3 NH 3 PbX 3 Nanorod Arrays for Light-Emitting Diodes*, Nano Letters 15, 5519 (2015).

[172] Y. Fu, F. Meng, M. B. Rowley, B. J. Thompson, M. J. Shearer, D. Ma, R. J. Hamers, J. C. Wright, and S. Jin, *Solution Growth of Single Crystal Methylammonium Lead Halide Perovskite Nanostructures for Optoelectronic and Photovoltaic Applications*, Journal of the American Chemical Society (2015).

[173] F. Fu, L. Kranz, S. Yoon, J. Löckinger, T. Jäger, J. Perrenoud, T. Feurer, C. Greuter, S. Bücheler, and A. N. Tiwari, *Controlled growth of PbI 2 nanoplates for rapid preparation of CH3NH3PbI3 in planar perovskite solar cells*, physica status solidi (a), n/a (2015).

[174] P. Tyagi, S. M. Arveson, and W. A. Tisdale, *Colloidal Organohalide Perovskite Nanoplatelets Exhibiting Quantum Confinement*, The Journal of Physical Chemistry Letters, 150923162617005 (2015).

[175] L. Dou, A. B. Wong, Y. Yu, M. Lai, N. Kornienko, N. S. Ginsberg, L.-W. Wang, A. P. Alivisatos, and P. Yang, *Atomically thin two-dimensional organic-inorganic hybrid perovskites*, Science 349, 1518 (2015).

[176] Y. Wang, Y. Shi, G. Xin, J. Lian, and J. Shi, *Two-Dimensional van der Waals Epitaxy Kinetics in a Three-Dimensional Perovskite Halide*, Crystal Growth & Design, 150923162617005 (2015).

[177] Q. A. Akkerman, S. G. Motti, A. R. Srimath Kandada, E. Mosconi, V. D’Innocenzo, G. Bertoni, S. Marras, B. A. Kamino, L. Miranda, F. De Angelis, A. Petrozza, M. Prato, and L. Manna, *Solution Synthesis Approach to Colloidal Cesium Lead Halide Perovskite Nanoplatelets with Monolayer-Level Thickness Control*, Journal of the American Chemical Society 138, 1010 (2016).

[178] S. W. Eaton, M. Lai, N. A. Gibson, A. B. Wong, L. Dou, J. Ma, L.-W. Wang, S. R. Leone, and P. Yang, *Lasing in robust cesium lead halide perovskite nanowires*, Proceedings of the National Academy of Sciences 113, 1993 (2016).

[179] Q. Liao, K. Hu, H. Zhang, X. Wang, J. Yao, and H. Fu, *Perovskite Microdisk Microlasers Self-Assembled from Solution*, Advanced Materials 27, 3405 (2015).

[180] J. Xing, X. Liu, Q. Zhang, S. T. Ha, Y. Yuan, C. Shen, T. C. Sum, and Q. Xiong, *Vapor Phase Synthesis of Organometal Halide Perovskite Nanowires for Tunable Room-Temperature Nanolasers*, Nano letters (2015).
REFERENCES

[181] Z. Wang, J. Liu, Z.-Q. Xu, Y. Xue, L. Jiang, J. Song, F. Huang, Y. Wang, Y. L. Zhong, Y. Zhang, Y.-B. Cheng, and Q. Bao, \textit{Wavelength-tunable waveguides based on polycrystalline organic–inorganic perovskite microwires}, Nanoscale \textbf{8}, 6258 (2016).

[182] L. Gu, M. M. Tavakoli, D. Zhang, Q. Zhang, A. Waleed, Y. Xiao, K.-H. Tsui, Y. Lin, L. Liao, J. Wang, and Z. Fan, \textit{3D Arrays of 1024-Pixel Image Sensors based on Lead Halide Perovskite Nanowires}, Advanced Materials \textbf{28}, 9713 (2016).

[183] D. H. Cao, C. C. Stoumpos, O. K. Farha, J. T. Hupp, and M. G. Kanatzidis, \textit{2D Homologous Perovskites as Light-Absorbing Materials for Solar Cell Applications}, Journal of the American Chemical Society \textbf{137}, 7843 (2015).

[184] I. C. Smith, E. T. Hoke, D. Solis-Ibarra, M. D. McGehee, and H. I. Karunadasa, \textit{A Layered Hybrid Perovskite Solar-Cell Absorber with Enhanced Moisture Stability}, Angewandte Chemie International Edition \textbf{53}, 11232 (2014).

[185] D. H. Cao, C. C. Stoumpos, O. K. Farha, J. T. Hupp, and M. G. Kanatzidis, \textit{Two-dimensional homologous perovskites as light absorbing materials for solar cell applications}, Journal of American Chemical Society (2015).

[186] J. Song, J. Li, X. Li, L. Xu, Y. Dong, and H. Zeng, \textit{Quantum Dot Light-Emitting Diodes Based on Inorganic Perovskite Cesium Lead Halides (\text{\text{ce}}CsPbX3)}, Advanced Materials \textbf{27}, 7162 (2015).

[187] W. Deng, X. Xu, X. Zhang, Y. Zhang, X. Jin, L. Wang, S.-T. Lee, and J. Jie, \textit{Organometal Halide Perovskite Quantum Dot Light-Emitting Diodes}, Advanced Functional Materials (2016).

[188] G. Li, Z.-K. Tan, D. Di, M. L. Lai, L. Jiang, J. H.-W. Lim, R. H. Friend, and N. C. Greenham, \textit{Efficient Light-Emitting Diodes Based on Nanocrystalline Perovskite in a Dielectric Polymer Matrix}, Nano Letters \textbf{15}, 2640 (2015).

[189] J. H. Noh, S. H. Im, J. H. Heo, T. N. Mandal, and S. I. Seok, \textit{Chemical management for colorful, efficient, and stable inorganic-organic hybrid nanostructured solar cells}, Nano Letters \textbf{13}, 1764 (2013).

[190] J. H. Heo, D. H. Song, H. J. Han, S. Y. Kim, J. H. Kim, D. Kim, H. W. Shin, T. K. Ahn, C. Wolf, T.-W. Lee, and S. H. Im, \textit{Planar CH3NH3PbI3 Perovskite Solar Cells with Constant 17.2% Average Power Conversion Efficiency Irrespective of the Scan Rate}, Advanced Materials \textbf{27}, 3464 (2015).

[191] S. Ryu, J. H. Noh, N. J. Jeon, Y. C. Kim, W. S. Yang, J. Seo, and S. I. Seok, \textit{Voltage Output of Efficient Perovskite Solar Cells with high Open-Circuit Voltage and Fill Factor}, Energy & Environmental Science \textbf{7}, 2614 (2014).

[192] E. Edri, S. Kirmayer, D. Cahen, and G. Hodes, \textit{High open-circuit voltage solar cells based on organic-inorganic lead bromide perovskite}, Journal of Physical Chemistry Letters \textbf{4}, 897 (2013).

[193] A. Dymshits, A. Rotem, and L. Etgar, \textit{High voltage in hole conductor free organo metal halide perovskite solar cells}, J. Mater. Chem. A \textbf{2}, 20776 (2014).

[194] M. Kulbak, D. Cahen, and G. Hodes, \textit{How Important Is the Organic Part of the Lead Halide Perovskite Photovoltaic Cells? Efficient CsPbBr3 Cells}, The Journal of Physical Chemistry Letters, 150610174239009 (2015).

[195] N. Yantara, S. Bhaumik, F. Yan, D. Sabba, H. A. Dewi, N. Mathews, P. P. Boix, H. V. Demir, and S. Mhaisalkar, \textit{Inorganic Halide Perovskites for Efficient Light-Emitting Diodes}, The Journal of Physical Chemistry Letters \textbf{6}, 4360 (2015).

[196] G. Grancini, A. R. Srimath Kandada, J. M. Frost, A. J. Barker, M. De Bastiani, M. Gandini, S. Marras, G. Lanzani, A. Walsh, and A. Petrozza, \textit{Role of microstructure in the electron–hole interaction of hybrid lead halide perovskites}, Nature Photonics \textbf{7}, 695.
REFERENCES

[197] J. S. Yun, A. Ho-Baillie, S. Huang, S. Woo, Y. Heo, J. Seidel, F. Huang, Y.-B. Cheng, and M. A. Green, The Benefit of Grain Boundaries in Organic-Inorganic Halide Planar Perovskite Solar Cells, The Journal of Physical Chemistry Letters (2015).

[198] J. Huang, Y. Shao, and Q. Dong, Organometal Trihalide Perovskite Single Crystals: A Next Wave of Materials for 25% Efficiency Photovoltaics and Applications Beyond?, Journal of Physical Chemistry Letters 6, 3218 (2015).

[199] P. Zhao, J. Xu, X. Dong, L. Wang, W. Ren, L. Bian, and A. Chang, Large-size CH3NH3PbBr3 Single Crystal: Growth and In Situ Characterization of the Photophysics Properties, The Journal of Physical Chemistry Letters (2015).

[200] H. Kunugita, T. Hashimoto, Y. Kiyota, Y. Udagawa, Y. Takeoka, Y. Nakamura, J. Sano, T. Matsushita, T. Kondo, T. Miyasaka, and K. Ema, Excitonic Feature in Hybrid Perovskite CH3NH3PbBr3 Single Crystals, Chemistry Letters 44, 852 (2015).

[201] Y. Yamada, T. Yamada, L. Q. Phuong, N. Murayama, H. Nishimura, A. Wakamiya, Y. Murata, and Y. Kanemitsu, Dynamic Optical Properties of CH3NH3PbI3 Single Crystals as Revealed by One- and Two-photon Excited Photoluminescence Measurements, Journal of the American Chemical Society 137, 10456 (2015).

[202] G. Grancini, V. D’Innocenzo, E. R. Dohner, N. Martino, A. R. Srimath Kandada, E. Mosconi, F. De Angelis, H. I. Karunadasa, E. T. Hoke, and A. Petrozza, CH3NH3PbI3 Perovskite Single Crystals: Surface Photophysics and its Interaction with the Environment, Chem. Sci. (2015).

[203] T. Zhang, M. Yang, E. E. Benson, Z. Li, J. van de Lagemaat, J. M. Luther, Y. Yan, K. Zhu, and Y. Zhao, A facile solvothermal growth of single crystal mixed halide perovskite CH3NH3Pb(Br1xClx)3, Chemical Communications 51, 7820 (2015).

[204] S. Brittman and E. C. Garnett, Measuring n and k at the Microscale in Single Crystals of CH3NH3PbBr3 Perovskite, The Journal of Physical Chemistry C 120, 616 (2016).

[205] D. J. Dingley and V. Randle, Microtexture determination by electron back-scatter diffraction, Journal of Materials Science 27, 4545 (1992).

[206] A. J. Schwartz, M. Kumar, B. L. Adams, and D. P. Field, editors, Electron Backscatter Diffraction in Materials Science, Springer US, Boston, MA, 2009.

[207] P. Schulz, E. Edri, S. Kirmayer, G. Hodes, D. Cahan, and A. Kahn, Interface energetics in organo-metal halide perovskite-based photovoltaic cells, Energy & Environmental Science 7, 1377 (2014).

[208] C.-C. Chueh, C.-Z. Li, and A. K.-Y. Jen, Recent Progress and Perspective in Solution-Processed Interfacial Materials for Efficient and Stable Polymer and Organometal Perovskite Solar Cells, Energy Environ. Sci. 8, 1160 (2015).

[209] T. Shi, W.-J. Yin, F. Hong, K. Zhu, and Y. Yan, Unipolar self-doping behavior in perovskite CH3NH3PbBr3, 2015.

[210] N. Kedem, T. M. Brenner, M. Kulbak, N. Schaefer, S. Levcenko, I. Levine, D. Abou-Ras, G. Hodes, and D. Cahan, Light-Induced Increase of Electron Diffusion Length in a p-n Junction Type CH3NH3PbBr3 Perovskite Solar Cell, The Journal of Physical Chemistry Letters 150610174034007 (2015).

[211] O. Knop, R. E. Wasylischen, M. A. White, T. S. Cameron, and M. J. M. V. Oort, Alkylammonium lead halides. Part 2. CH3NH3PbX3 (X = Cl, Br, I) perovskites: cuboctahedral halide cages with isotropic cation reorientation, Canadian Journal of Chemistry 68, 412 (1990).

[212] P. Khoram, S. Britttman, W. Dzik, J. Reek, and E. Garnett, Growth and Characterization of PDMS-Stamped Halide Perovskite Single Microcrystals, Journal of Physical
REFERENCES

Chemistry C 120 (2016).
[213] Bruker, 2014.
[214] G. M. Sheldrick, SADABS: Area-Detector Absorption Correction, Universität Göttingen, Germany, 1999.
[215] G. M. Sheldrick, SHELXT, Universität Göttingen, Germany, 2012.
[216] A. Goldmann, editor, Subvolume B, volume 23b of Landolt-Börnstein - Group III Condensed Matter, Springer-Verlag, Berlin/Heidelberg, 1994.
[217] S. M. Sze and K. Kwo, Physics of Semiconductor Devices, Number 1, 2007.
[218] G. F. Burkhard, E. T. Hoke, and M. D. McGehee, Accounting for Interference, Scattering, and Electrode Absorption to Make Accurate Internal Quantum Efficiency Measurements in Organic and Other Thin Solar Cells, Advanced Materials 22, 3293 (2010).
[219] D. W. Lynch, C. G. Olson, and J. H. Weaver, Optical properties of Ti, Zr, and Hf from 0.15 to 30 eV, Physical Review B 11, 3617 (1975).
[220] D. W. de Quilettes et al., Impact of microstructure on local carrier lifetime in perovskite solar cells, Science 348, 683 (2015).
[221] K. Wojciechowski, S. D. Stranks, A. Abate, G. Sadoughi, A. Sadhanala, N. Kopidakis, G. Rumbles, C.-Z. Li, R. H. Friend, A. K.-Y. Jen, and H. J. Snaith, Heterojunction Modification for Highly Efficient Organic-Inorganic Perovskite Solar Cells, ACS Nano 8, 12701 (2014).
[222] B. Conings, J. Drijkoningen, N. Gauquelin, A. Babayigit, J. D’Haen, L. D’Olieslaeger, A. Ethirajan, J. Verbeeck, J. Manca, E. Mosconi, F. De Angelis, and H. G. Boyen, Intrinsic Thermal Instability of Methylammonium Lead Trihalide Perovskite, Advanced Energy Materials 5, 1 (2015).
[223] G. E. Eperon, S. N. Habisreutinger, T. Leijtens, B. J. Bruiniaers, J. J. Van Franeker, D. W. Dequilettes, S. Pathak, R. J. Sutton, G. Grancini, D. S. Ginger, R. A. J. Janssen, A. Petrozza, and H. J. Snaith, The Importance of Moisture in Hybrid Lead Halide Perovskite Thin Film Fabrication, ACS Nano 9, 9380 (2015).
[224] E. T. Hoke, D. I. Slotcavage, E. R. Dohner, A. R. Bowring, H. I. Karunadasa, and M. D. McGehee, Reversible photo-induced trap formation in mixed-halide hybrid perovskites for photovoltaics, Chemical Science 6, 613 (2015).
[225] T. Leijtens, G. E. Eperon, N. K. Noel, S. N. Habisreutinger, A. Petrozza, and H. J. Snaith, Stability of metal halide perovskite solar cells, Advanced Energy Materials 5, 1500963 (2015).
[226] C. Eames, J. M. Frost, P. R. F. Barnes, B. C. O’Regan, A. Walsh, and M. S. Islam, Ionic transport in hybrid lead iodide perovskite solar cells, Nature Communications 6, 7497 (2015).
[227] J. Yang, B. D. Siempelkamp, D. Liu, and T. L. Kelly, An Investigation of CH3NH3PbI3 Degradation Rates and Mechanisms in Controlled Humidity Environments Using in situ Techniques, Nature nano, Advance (2015).
[228] S. Meloni, T. Moehl, W. Tress, M. Frankevičius, M. Saliba, Y. H. Lee, P. Gao, M. K. Nazeeruddin, S. M. Zakeeruddin, U. Rothlisberger, and M. Graetzel, Ionic polarization-induced current–voltage hysteresis in CH3NH3PbX3 perovskite solar cells, Nature Communications 7, 1 (2016).
[229] W. Tress, N. Marinova, T. Moehl, S. M. Zakeeruddin, M. K. Nazeeruddin, and M. Grätzel, Understanding the rate-dependent J–V hysteresis, slow time component, and aging in CH3NH3PbI3 perovskite solar cells: the role of a compensated electric field, Energy Environ. Sci. 8, 995 (2015).
[230] A. Walsh, D. O. Scanlon, S. Chen, X. G. Gong, and S. H. Wei, Self-regulation
mechanism for charged point defects in hybrid halide perovskites, Angewandte Chemie - International Edition 54, 1791 (2015).

[231] M. Cherry, M. Islam, and C. Catlow, Oxygen Ion Migration in Perovskite-Type Oxides, 1995.

[232] J.-P. Correa-Baena, A. Abate, M. Saliba, W. Tress, T. Jesper Jacobsson, M. Grätzel, and A. Hagfeldt, The rapid evolution of highly efficient perovskite solar cells, Energy Environ. Sci. 10, 710 (2017).

[233] J. Yan, X. Ke, Y. Chen, A. Zhang, and B. Zhang, Effect of modulating the molar ratio of organic to inorganic content on morphology, optical absorption and photoluminescence of perovskite CH3NH3PbBr3 films, Applied Surface Science 351, 1191 (2015).

[234] Y. Yuan, J. Chae, Y. Shao, Q. Wang, Z. Xiao, A. Centrone, and J. Huang, Photovoltaic Switching Mechanism in Lateral Structure Hybrid Perovskite Solar Cells, Advanced Energy Materials 5, 1 (2015).

[235] D. W. DeQuilettes, W. Zhang, V. M. Burlakov, D. J. Graham, T. Leijtens, A. Osherov, V. Bulović, H. J. Snaith, D. S. Ginger, and S. D. Stranks, Photo-induced halide redistribution in organic–inorganic perovskite films, Nature Communications 7, 1 (2016).

[236] C. Li, S. Tscheuschner, F. Paulus, P. E. Hopkinson, J. Kieling, A. Khler, Y. Vaynzof, and S. Huettnern, Iodine Migration and its Effect on Hysteresis in Perovskite Solar Cells, Advanced Materials 28, 2446 (2016).

[237] A. Benninghoven, Chemical Analysis of Inorganic and Organic Surfaces and Thin Films by Static Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS), Angewandte Chemie International Edition in English 33, 1023 (1994).

[238] T. Glatzer, C. Müller, M. Sendner, C. Krekeler, O. E. Semeniouk, T. D. Hull, O. Yaffe, J. S. Owen, W. Kowalsky, A. Pucci, and R. Lovrincic, Infrared Spectroscopic Study of Vibrational Modes in Methylammonium Lead Halide Perovskites, The Journal of Physical Chemistry Letters 6, 2913 (2015).

[239] N. Klein-Kedem, D. Cahen, and G. Hodes, Effects of Light and Electron Beam Irradiation on Halide Perovskites and Their Solar Cells, Accounts of Chemical Research 49, 347 (2016).

[240] Y. Luo, S. Gamliel, S. Nijem, S. Aharon, M. Holt, B. Stripe, V. Rose, M. I. Bertoni, L. Etgar, and D. P. Fenning, Spatially Heterogeneous Chlorine Incorporation in Organic-Inorganic Perovskite Solar Cells, Chemistry of Materials 28, 6536 (2016).

[241] R. P. Winarski, M. V. Holt, V. Rose, P. Fuesz, D. Carbaugh, C. Benson, D. Shu, D. Kline, G. B. Stephenson, I. McNulty, and J. Maser, A hard X-ray nanoprobe beamline for nanoscale microscopy, Journal of Synchrotron Radiation 19, 1056 (2012).

[242] M. Stuckelberger, B. West, T. Nietzold, B. Lai, J. M. Maser, V. Rose, and M. I. Bertoni, Review: Engineering Solar Cells Based on Correlative X-Ray Microscopy, Journal of Materials Research 32, 1825 (2017).

[243] S. Mastroianni, F. D. Heinz, J.-H. Im, W. Veurm, M. Padilla, M. C. Schubert, U. Würfel, M. Grätzel, N.-G. Park, and A. Hinsch, Analysing the effect of crystal size and structure in highly efficient CH3NH3PbI3 perovskite solar cells by spatially resolved photo- and electroluminescence imaging, Nanoscale , 19653 (2015).

[244] A. M. Soufiani, Z. Hameiri, S. Meyer, S. Lim, M. J. Y. Tayebjee, J. S. Yun, A. Ho-Baillie, G. J. Conibeer, L. Spiccia, and M. A. Green, Lessons Learnt from Spatially Resolved Electro- and Photoluminescence Imaging: Interfacial Delamination in CH3NH3PbI3 Planar Perovskite Solar Cells upon Illumination, Advanced Energy Materials , 1 (2016).

[245] A. M. Soufiani, M. J. Y. Tayebjee, S. Meyer, A. Ho-Baillie, J. Sung Yun, R. W. McQueen,
REFERENCES

L. Spiccia, M. A. Green, and Z. Hameiri, Electro- and photoluminescence imaging as fast screening technique of the layer uniformity and device degradation in planar perovskite solar cells, Journal of Applied Physics 120 (2016).

[246] M. A. Green, Radiative efficiency of state-of-the-art photovoltaic cells, Prog. Photovolt: Res. Appl. 20, 472 (2012).

[247] J. Li, Q. Dong, N. Li, and L. Wang, Direct Evidence of Ion Diffusion for the Silver-Electrode-Induced Thermal Degradation of Inverted Perovskite Solar Cells, Advanced Energy Materials, 1 (2017).

[248] K. Ando, A. Yamamoto, and M. Yamaguchi, Surface Band Bending Effects on Photoluminescence Intensity in n-InP Schottky and MIS Diodes, Japanese Journal of Applied Physics 20, 1107 (1981).

[249] I. E. Beckers, U. Fiedeler, S. Siebentritt, and M. C. Lux-Steiner, Voltage dependent electromodulated photoluminescence of chalcopyrite solar cells, Journal of Physics and Chemistry of Solids 64, 2031 (2003).

[250] N. N. Winogradoff, Field Control of the Quantum Efficiency of Radiative Recombination in Semiconductors, Physical Review 138, A1562 (1965).

[251] J. Yan, B. Zhang, Y. Chen, A. Zhang, and X. Ke, Improving the Photoluminescence Properties of Perovskite CH3NH3PbBr3-xClx Films by Modulating Organic Cation and Chlorine Concentrations, ACS Applied Materials and Interfaces 8, 12756 (2016).

[252] K. Zheng, M. Abdellah, Q. Zhu, Q. Kong, G. Jennings, C. A. Kurtz, M. E. Messing, Y. Niu, D. J. Gosztola, M. J. Al-Marri, X. Zhang, T. Pullerits, and S. E. Canton, Direct Experimental Evidence for Photoinduced Strong-Coupling Polaron in Organolead Halide Perovskite Nanoparticles, The Journal of Physical Chemistry Letters 7, 4535 (2016).

[253] J. Haruyama, K. Sodeyama, L. Han, and Y. Tateyama, First-principles study of ion diffusion in perovskite solar cell sensitizers, Journal of the American Chemical Society 137, 10048 (2015).

[254] J.-H. Yang, W.-J. Yin, J.-S. Park, and S.-H. Wei, Fast self-diffusion of ions in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>: the interstitially mechanism versus vacancy-assisted mechanism, J. Mater. Chem. A 4, 13105 (2016).

[255] Z. Deng, B. Radhakrishnan, and S. P. Ong, Rational Composition Optimization of the Lithium-Rich Li<sub>1–x</sub>OCl<sub>x</sub> Anti-Perovskite Superionic Conductors, Chemistry of Materials 27, 3749 (2015).

[256] H. Mashiyama, Y. Kawamura, H. Kasano, T. Asahi, Y. Noda, and H. Kimura, Disordered Configuration of Methylammonium of CH3NH3PbBr3 Determined by Single Crystal Neutron Diffractometry, Ferroelectrics 348, 182 (2007).

[257] T. J. Jacobsson, J.-P. Correa-Baena, E. Halvani Anaraki, B. Philippe, S. D. Stranks, M. E. F. Bouduban, W. Tress, K. Schenk, J. Teuscher, J.-E. Moser, H. Rensmo, and A. Hagfeldt, Unreacted PbI<sub>2</sub> as a Double-Edged Sword for Enhancing the Performance of Perovskite Solar Cells, Journal of the American Chemical Society 138, 10331 (2016).

[258] G. Kresse and J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, Physical Review B 54, 11169 (1996).

[259] P. E. Blöchl, Projector augmented-wave method, Physical Review B 50, 17953 (1994).

[260] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized Gradient Approximation Made Simple, Physical Review Letters 77, 3865 (1996).

[261] S. P. Ong, W. D. Richards, A. Jain, G. Hautier, M. Kocher, S. Cholia, D. Gunter, V. L. Chevrier, K. A. Persson, and G. Ceder, Python Materials Genomics (pymatgen): A robust, open-source python library for materials analysis, Computational Materials
REFERENCES

Science **68**, 314 (2013).

[262] T. M. Brenner, D. A. Egger, L. Kronik, G. Hodes, and D. Cahen, *Hybrid organic—-inorganic perovskites: low-cost semiconductors with intriguing charge-transport properties*, Nature Reviews Materials **1**, 15007 (2016).

[263] S. A. Mann, R. R. Grote, R. M. Osgood, A. Alù, and E. C. Garnett, *Opportunities and Limitations for Nanophotonic Structures To Exceed the Shockley–Queisser Limit*, ACS Nano **10**, 8620 (2016).

[264] M. L. Brongersma, Y. Cui, and S. Fan, *Light management for photovoltaics using high-index nanostructures*, Nature Materials **13**, 451 (2014).

[265] V. E. Ferry, M. A. Verschuuren, H. B. T. Li, E. Verhagen, R. J. Walters, R. E. I. Schropp, H. A. Atwater, and A. Polman, *Light trapping in ultrathin plasmonic solar cells*, Optics Express **18**, A237 (2010).

[266] S. A. Mann and E. C. Garnett, *Extreme Light Absorption in Thin Semiconductor Films Wrapped around Metal Nanowires*, Nano Letters **13**, 3173 (2013).

[267] E. Garnett and P. Yang, *Light Trapping in Silicon Nanowire Solar Cells*, Nano Letters **10**, 1082 (2010).

[268] J. Wallentin, N. Anttu, D. Asoli, M. Huffman, I. rAberg, M. H. Magnusson, G. Siefer, P. Fuss-Kailuweit, F. Dimroth, B. Witzigmann, H. Q. Xu, L. Samuelson, K. Deppert, and M. T. Borgström, *InP nanowire array solar cells achieving 13.8% efficiency by exceeding the ray optics limit*, Science **339**, 1057 (2013).

[269] A. Polman and H. a. Atwater, *Photonic design principles for ultrahigh-efficiency photovoltaics*, 2012.

[270] Z. Yu, A. Raman, and S. Fan, *Fundamental limit of nanophotonic light trapping in solar cells*, Proceedings of the National Academy of Sciences **107**, 17491 (2010).

[271] S. A. Mann and E. C. Garnett, *Resonant nanophotonic spectrum splitting for ultrathin multijunction solar cells*, ACS Photonics **2**, 816 (2015).

[272] D. Zhang, Y. Yu, Y. Bekenstein, A. B. Wong, A. P. Alivisatos, and P. Yang, *Ultrathin Colloidal Cesium Lead Halide Perovskite Nanowires*, Journal of the American Chemical Society **138**, 13155 (2016).

[273] A. A. Petrov, N. Pellet, J. Y. Seo, N. A. Belich, D. Y. Kovalev, A. V. Shevelkov, E. A. Goodilin, S. M. Zakeeruddin, A. B. Tarasov, and M. Graetzel, *New Insight into the Formation of Hybrid Perovskite Nanowires via Structure Directing Adducts*, Chemistry of Materials **29**, 587 (2017).

[274] K. Park, J. W. Lee, J. D. Kim, N. S. Han, D. M. Jang, S. Jeong, J. Park, and J. K. Song, *Light–Matter Interactions in Cesium Lead Halide Perovskite Nanowire Lasers*, The Journal of Physical Chemistry Letters **7**, 3703 (2016).

[275] H. Deng, D. Dong, K. Qiao, L. Bu, B. Li, D. Yang, H.-E. Wang, Y. Cheng, Z. Zhao, J. Tang, and H. Song, *Growth, patterning and alignment of organolead iodide perovskite nanowires for optoelectronic devices*, Nanoscale **7**, 4163 (2015).

[276] M. J. Ashley, M. N. O’Brien, K. R. Hedderick, J. A. Mason, M. B. Ross, and C. A. Mirkin, *Templated Synthesis of Uniform Perovskite Nanowire Arrays*, Journal of the American Chemical Society **138**, 10096 (2016).

[277] A. Waleed, M. M. Tavakoli, L. Gu, Z. Wang, D. Zhang, A. Manikandan, Q. Zhang, R.-J. Zhang, Y.-L. Chueh, and Z. Fan, *Lead-Free Perovskite Nanowire Array Photodetectors with Drastically Improved Stability in Nanoengineering Templates*, Nano Letters **17**, 523 (2017).

[278] M. M. Tavakoli, A. Waleed, L. Gu, D. Zhang, R. Tavakoli, B. Lei, W. Su, F. Fang, and Z. Fan, *A non-catalytic vapor growth regime for organohalide perovskite nanowires*
REFERENCES

using anodic aluminum oxide templates, Nanoscale 9, 5828 (2017).

[279] E. Lafalce, C. Zhang, Y. Zhai, D. Sun, and Z. V. Vardeny, Enhanced emissive and lasing characteristics of nano-crystalline MAPbBr3 films grown via anti-solvent precipitation, Journal of Applied Physics 120, 143101 (2016).

[280] L. Wen, R. Xu, Y. Mi, and Y. Lei, Multiple nanostructures based on anodized aluminium oxide templates, Nature Nanotechnology 12, 244 (2017).

[281] J. W. Elam, D. Routkevitch, P. P. Mardilovich, and S. M. George, Conformal coating on ultrahigh-aspect-ratio nanopores of anodic alumina by atomic layer deposition, Chemistry of Materials 15, 3507 (2003).

[282] W. Lee and S.-J. Park, Porous Anodic Aluminum Oxide: Anodization and Templated Synthesis of Functional Nanostructures, Chemical Reviews 114, 7487 (2014).

[283] H. Masuda, A. Abe, M. Nakao, A. Yokoo, T. Tamamura, and K. Nishio, Ordered mosaic nanocomposites in anodic porous alumina, Advanced Materials 15, 161 (2003).

[284] T. Yanagishita, M. Sasaki, K. Nishio, and H. Masuda, Carbon Nanotubes with a Triangular Cross-section, Fabricated Using Anodic Porous Alumina as the Template, Advanced Materials 16, 429 (2004).

[285] J. T. Smith, Q. Hang, A. D. Franklin, D. B. Janes, and T. D. Sands, Highly ordered diamond and hybrid triangle-diamond patterns in porous anodic alumina thin films, Applied Physics Letters 93, 043108 (2008).

[286] H. Robatjazi, S. M. Bahauddin, L. H. Macfarlan, S. Fu, and I. Thomann, Ultrathin AAO Membrane as a Generic Template for Sub-100 nm Nanostructure Fabrication, Chemistry of Materials 28, 4546 (2016).

[287] M. Tian, S. Xu, J. Wang, N. Kumar, E. Wertz, Q. Li, P. M. Campbell, M. H. Chan, and T. E. Mallouk, Penetrating the oxide barrier in situ and separating freestanding porous anodic alumina films in one step, Nano Letters 5, 697 (2005).

[288] Y. Guo, K. Shoyama, W. Sato, Y. Matsuo, K. Inoue, K. Harano, C. Liu, H. Tanaka, and E. Nakamura, Chemical Pathways Connecting Lead(II) Iodide and Perovskite via Polymeric Plumbate(II) Fiber, Journal of the American Chemical Society 137, 15907 (2015).

[289] N. J. Jeon, J. H. Noh, Y. C. Kim, W. S. Yang, S. Ryu, and S. I. Seok, inorganic – organic hybrid perovskite solar cells, 13, 897 (2014).

[290] B. Jeong, I. Hwang, S. H. Cho, E. H. Kim, S. Cha, J. Lee, H. S. Kang, S. M. Cho, H. Choi, and C. Park, Solvent-Assisted Gel Printing for Micropatterning Thin Organic–Inorganic Hybrid Perovskite Films, ACS Nano 10, 9026 (2016).

[291] S. T. Williams, C. C. Chueh, and A. K.-Y. Jen, Navigating Organo-Lead Halide Perovskite Phase Space via Nucleation Kinetics toward a Deeper Understanding of Perovskite Phase Transformations and Structure-Property Relationships, 2015.

[292] M. Ko, S. H. Baek, B. Song, J. W. Kang, S. A. Kim, and C. H. Cho, Periodically Diameter-Modulated Semiconductor Nanowires for Enhanced Optical Absorption, Advanced Materials 28, 2504 (2016).

[293] L. Cao, J. S. White, J.-S. Park, J. A. Schuller, B. M. Clemens, and M. L. Brongersma, Engineering light absorption in semiconductor nanowire devices, Nature Materials 8, 643 (2009).

[294] D. I. Woodward and I. M. Reaney, Electron diffraction of tilted perovskites, 2005.

[295] Y. Yu, D. Zhang, C. Kisielowski, L. Dou, N. Kornienko, Y. Bekenstein, A. B. Wong, A. P. Alivisatos, and P. Yang, Atomic Resolution Imaging of Halide Perovskites, Nano Letters 16, 7530 (2016).

[296] S. A. Mann, B. Sciacca, Y. Zhang, J. Wang, E. Kontoleta, H. Liu, and E. C.
Garnett, *Integrating Sphere Microscopy for Direct Absorption Measurements of Single Nanostructures*, ACS Nano **11**, 1412 (2017).

[297] S. A. Mann, S. Z. Oener, A. Cavalli, J. E. Haverkort, E. P. Bakkers, and E. C. Garnett, *Quantifying losses and thermodynamic limits in nanophotonic solar cells*, Nature Nanotechnology **11**, 1071 (2016).

[298] Y. Luo, P. Khoram, S. Brittmann, Z. Zhu, B. Lai, S. P. Ong, E. C. Garnett, and D. P. Fenning, *Direct Observation of Halide Migration and its Effect on the Photoluminescence of Methylammonium Lead Bromide Perovskite Single Crystals*, Advanced Materials **29**, 1703451 (2017).

[299] H. Tsai, W. Nie, Y.-H. Lin, J. C. Blancon, S. Tretiak, J. Even, G. Gupta, P. M. Ajayan, and A. D. Mohite, *Effect of Precursor Solution Aging on the Crystallinity and Photovoltaic Performance of Perovskite Solar Cells*, Advanced Energy Materials **7**, 1602159 (2017).

[300] G. Namkoong, A. A. Mamun, T. T. Ava, K. Zhang, and H. Baumgart, *Impact of perovskite precursor solution temperature on charge carrier dynamics and photovoltaic performance of perovskite based solar cells*, Organic Electronics: physics, materials, applications **42**, 228 (2017).

[301] B. E. Cohen and L. Etgar, *Parameters that control and influence the organo-metal halide perovskite crystallization and morphology*, Frontiers of Optoelectronics **9**, 44 (2016).

[302] J. Huang, X. Yu, J. Xie, D. Xu, Z. Tang, C. Cui, and D. Yang, *Ambient Engineering for High-Performance Organic-Inorganic Perovskite Hybrid Solar Cells*, ACS Applied Materials and Interfaces **8**, 21505 (2016).

[303] J. Shi, X. Xu, D. Li, and Q. Meng, * Interfaces in Perovskite Solar Cells*, Small (2015).

[304] N. K. Noel, A. Abate, S. D. Stranks, E. S. Parrott, V. M. Burlakov, A. Goriely, and H. J. Snaith, *Enhanced photoluminescence and solar cell performance via Lewis base passivation of organic-inorganic lead halide perovskites*, ACS Nano **8**, 9815 (2014).

[305] A. Abate, M. Saliba, D. J. Hollman, S. D. Stranks, K. Wojciechowski, R. Avolio, G. Grancini, A. Petrozza, and H. J. Snaith, *Supramolecular halogen bond passivation of organic-inorganic halide perovskite solar cells*, Nano Letters **14**, 3247 (2014).

[306] K. Oura, M. Katayama, A. V. Zотов, V. G. Lifshits, and A. A. Saranin, *Surface Science, Advanced Texts in Physics*, Springer Berlin Heidelberg, Berlin, Heidelberg, 2003.

[307] P. Cui, P. Fu, D. Wei, M. Li, D. Song, X. Yue, Y. Li, Z. Zhang, Y. Li, and J. M. Mbengue, *Reduced surface defects of organometallic perovskite by thermal annealing for highly efficient perovskite solar cells*, RSC Advances **5**, 75622 (2015).

[308] H.-H. Fang, S. Adjokatse, H. Wei, J. Yang, G. R. Blake, J. Huang, J. Even, and M. A. Loi, *Ultrahigh sensitivity of methylammonium lead tribromide perovskite single crystals to environmental gases*, Science Advances **2**, e1600534 (2016).

[309] R. S. Bonilla, C. Reichel, M. Hermle, and P. R. Wilshaw, *Electric Field Effect Surface Passivation for Silicon Solar Cells*, Solid State Phenomena **205-206**, 346 (2013).

[310] A. G. Aberle, *Surface passivation of crystalline silicon solar cells: a review*, Progress in Photovoltaics: Research and Applications **8**, 473 (2000).

[311] A. G. Aberle, *Overview on SiN surface passivation of crystalline silicon solar cells*, Solar Energy Materials and Solar Cells **65**, 239 (2001).

[312] W. Soppe, H. Rieffe, and A. Weeber, *Bulk and surface passivation of silicon solar cells accomplished by silicon nitride deposited on industrial scale by microwave PECVD*, Progress in Photovoltaics: Research and Applications **13**, 551 (2005).

[313] J. Schmidt, F. Werner, B. Veith, D. Zielke, S. Steingrube, P. Altermatt, S. Gatz, T. Dullweber, and R. Brendel, *Advances in the Surface Passivation of Silicon Solar Cells,
REFERENCES

Energy Procedia 15, 30 (2012).

[314] M. L. Huang, Y. C. Chang, C. H. Chang, Y. J. Lee, P. Chang, J. Kwo, T. B. Wu, and M. Hong, *Surface passivation of III-V compound semiconductors using atomic-layer-deposition-grown AL2O3*, Applied Physics Letters 87, 252104 (2005).

[315] J. Xu, A. Buin, A. H. Ip, W. Li, O. Voznyy, R. Comin, M. Yuan, S. Jeon, Z. Ning, J. J. McDowell, P. Kanjanaboos, J.-P. Sun, X. Lan, L. N. Quan, D. H. Kim, I. G. Hill, P. Maksymovych, and E. H. Sargent, *Perovskite–fullerene hybrid materials suppress hysteresis in planar diodes*, Nature Communications 6, 7081 (2015).

[316] Y. Shao, Z. Xiao, C. Bi, Y. Yuan, and J. Huang, *Origin and elimination of photocurrent hysteresis by fullerene passivation in CH3NH3PbI3 planar heterojunction solar cells*, Nature Communications 5, 5784 (2014).

[317] J. Peng, Y. Wu, W. Ye, D. A. Jacobs, H. Shen, X. Fu, Y. Wan, T. Duong, N. Wu, C. Barugkin, H. T. Nguyen, D. Zhong, J. Li, T. Lu, Y. Liu, M. N. Lockrey, K. J. Weber, K. R. Catchpole, and T. P. White, *Interface passivation using ultrathin polymer–fullerene films for high-efficiency perovskite solar cells with negligible hysteresis*, Energy & Environmental Science 10, 1792 (2017).

[318] H. Li, L. Tao, F. Huang, Q. Sun, X. Zhao, J. Han, Y. Shen, and M. Wang, *Enhancing efficiency of perovskite solar cells via surface passivation with graphene oxide interlayer*, ACS Applied Materials & Interfaces, acsami.7b10773 (2017).

[319] L. Wang, C. McCleese, A. Kovalsky, Y. Zhao, and C. Burda, *Femtosecond Time-Resolved Transient Absorption Spectroscopy of CH3 NH3 PbI 3 Peroxide Films: Evidence for Passivation Effect of PbI 2*, Journal of the American Chemical Society 136, 12205 (2014).

[320] Q. Chen, H. Zhou, T.-b. Song, S. Luo, and Z. Hong, *Controllable self-induced passivation of hybrid lead iodide perovskites toward high performance solar cells Controllable self-induced passivation of hybrid lead iodide perovskites toward high performance solar cells*, Nano Letters 14, 4158 (2014).

[321] T. Supasai, N. Rujisamphan, K. Ullrich, A. Chemseddine, T. Dittrich, T. Supasai, N. Rujisamphan, K. Ullrich, A. Chemseddine, and T. Dittrich, *Formation of a passivating CH3NH3PbI3 / PbI2 interface during moderate heating of CH3NH3PbI3 layers*, Journal of the American Chemical Society 136, 12205 (2014).

[322] Y. C. Kim, N. J. Jeon, J. H. Noh, W. S. Yang, J. Seo, J. S. Yun, A. Ho-Baillie, S. Huang, M. A. Green, J. Seidel, T. K. Ahn, and S. I. Seok, *Beneficial Effects of PbI 2 Incorporated in Organo-Lead Halide Perovskite Solar Cells*, Advanced Energy Materials 6, 1502104 (2016).

[323] Z. Ren, A. Ng, Q. Shen, H. C. Gokkaya, J. Wang, L. Yang, W.-K. Yiu, G. Bai, A. B. Djurišić, W. W.-f. Leung, J. Hao, W. K. Chan, and C. Surya, *Thermal Assisted Oxygen Annealing for High Efficiency Planar CH3NH3PbI3 Perovskite Solar Cells*, Scientific Reports 4, 6752 (2015).

[324] H. Wei, Y. Fang, P. Mulligan, W. Chuirazzi, H.-H. Fang, C. Wang, B. R. Ecker, Y. Gao, M. A. Loi, L. Cao, and J. Huang, *Sensitive X-ray detectors made of methylammonium lead tribromide perovskite single crystals*, Nature Photonics *advance on* (2016).

[325] R. Brenes, D. Guo, A. Osherov, N. K. Noel, C. Eames, E. M. Hutter, S. K. Pathak, F. Niroi, R. H. Friend, M. S. Islam, H. J. Snaith, V. Bulović, T. J. Savenije, and S. D. Stranks, *Metal Halide Perovskite Polycrystalline Films Exhibiting Properties of Single Crystals*, Joule 1, 155 (2017).

[326] X. Dong, H. Hu, B. Lin, J. Ding, and N. Yuan, *The effect of ALD-Zno layers on the formation of CH 3 NH 3 PbI 3 with different perovskite precursors and sintering
temperatures, Chem. Commun. 50, 14405 (2014).

[327] C. Y. Chang, K. T. Lee, W. K. Huang, H. Y. Siao, and Y. C. Chang, High-Performance, Air-Stable, Low-Temperature Processed Semitransparent Perovskite Solar Cells Enabled by Atomic Layer Deposition, Chemistry of Materials 27, 5122 (2015).

[328] A. Hultqvist, K. Aitola, K. Sveinbjörnsson, Z. Saki, F. Larsson, T. Törndahl, E. Johansson, G. Boschloo, and M. Edoff, Atomic Layer Deposition of Electron Selective SnOx and ZnO Films on Mixed Halide Perovskite: Compatibility and Performance, ACS Applied Materials and Interfaces 9, 29707 (2017).

[329] H. Si, Q. Liao, Z. Zhang, Y. Li, X. Yang, G. Zhang, Z. Kang, and Y. Zhang, An innovative design of perovskite solar cells with Al2O3 inserting at ZnO/perovskite interface for improving the performance and stability, Nano Energy 22, 223 (2016).

[330] D. Koushik, W. J. H. Verhees, Y. Kuang, S. Veenstra, D. Zhang, M. A. Verheijen, M. Creatore, and R. E. I. Schropp, High-efficiency humidity-stable planar perovskite solar cells based on atomic layer architecture, Energy Environ. Sci. 10, 91 (2017).

[331] D. Koushik, W. J. Verhees, D. Zhang, Y. Kuang, S. Veenstra, M. Creatore, and R. E. Schropp, Atomic Layer Deposition Enabled Perovskite/PEDOT Solar Cells in a Regular n–i–p Architectural Design, Advanced Materials Interfaces 4 (2017).

[332] M. Kot, C. Das, Z. Wang, K. Henkel, Z. Rouissi, K. Wojciechowski, H. J. Snaith, and D. Schmeisser, Room-Temperature Atomic Layer Deposition of Al2O3: Impact on Efficiency, Stability and Surface Properties in Perovskite Solar Cells, ChemSusChem 9, 3401 (2016).

[333] G. W. P. Adhyaksa, L. W. Veldhuizen, Y. Kuang, S. Brittain, R. E. I. Schropp, and E. C. Garnett, Carrier Diffusion Lengths in Hybrid Perovskites: Processing, Composition, Aging, and Surface Passivation Effects, Chemistry of Materials 28, 5259 (2016).

[334] X. Dong, X. Fang, M. Lv, B. Lin, S. Zhang, J. Ding, and N. Yuan, Improvement of the humidity stability of organic–inorganic perovskite solar cells using ultrathin Al 2 O 3 layers prepared by atomic layer deposition, Journal of Materials Chemistry A 3, 5360 (2015).

[335] V. Zardetto, B. L. Williams, A. Perrotta, F. Di Giacomo, M. A. Verheijen, R. Andriessen, W. M. M. Kessels, and M. Creatore, Atomic layer deposition for perovskite solar cells: research status, opportunities and challenges, Sustainable Energy Fuels 1, 30 (2017).

[336] F. Léonard, A. A. Talin, B. S. Swartzentruber, and S. T. Picraux, Diameter-Dependent Electronic Transport Properties of Au-Catalyst/Ge-Nanowire Schottky Diodes, 106805, 1 (2009).

[337] O. Demichel, V. Calvo, A. Besson, P. Noé, B. Salem, N. Pauc, F. Oehler, P. Gentile, and N. Magnée, Surface recombination velocity measurements of efficiently passivated gold-catalyzed silicon nanowires by a new optical method, Nano Letters 10, 2323 (2010).

[338] Y. Dan, K. Seo, K. Takei, J. H. Meza, A. Javey, and K. B. Crozier, Dramatic reduction of surface recombination by in situ surface passivation of silicon nanowires, Nano Letters 11, 2527 (2011).

[339] H. J. Joyce, J. Wong-Leung, C. K. Yong, C. J. Docherty, S. Paiman, Q. Gao, H. H. Tan, C. Jagadish, J. Lloyd-Hughes, L. M. Herz, and M. B. Johnston, Ultralow surface recombination velocity in InP nanowires probed by terahertz spectroscopy, Nano Letters 12, 5325 (2012).

[340] Y. Li, F. Qian, J. Xiang, and C. M. Lieber, Nanowire electronic and optoelectronic devices, Materials Today 9, 18 (2006).

[341] E. C. Garnett, M. L. Brongersma, Y. Cui, and M. D. McGehee, Nanowire Solar Cells,
[342] T. Wang, B. Daiber, J. M. Frost, S. Mann, E. Garnett, A. Walsh, and B. Ehrler, Indirect to direct bandgap transition in methylammonium lead halide perovskite, Energy Environ. Sci. 10, 509 (2016).

[343] S. Chen, X. Wen, S. Huang, F. Huang, Y.-B. Cheng, M. Green, and A. Ho-Baillie, Light Illumination Induced Photoluminescence Enhancement and Quenching in Lead Halide Perovskite, Solar RRL 1, 1600001 (2017).

[344] Y. Yang, Y. Yan, M. Yang, S. Choi, K. Zhu, J. M. Luther, and M. C. Beard, Low surface recombination velocity in solution-grown CH3NH3PbBr3 perovskite single crystal, Nature Communications 6, 7961 (2015).

[345] B. Wu, H. T. Nguyen, Z. Ku, G. Han, D. Giovanni, N. Mathews, H. J. Fan, and T. C. Sum, Discerning the Surface and Bulk Recombination Kinetics of Organic–Inorganic Halide Perovskite Single Crystals, Advanced Energy Materials 6, 1 (2016).

[346] Y. Yang, M. Yang, Z. Li, R. Crisp, K. Zhu, and M. C. Beard, Comparison of Recombination Dynamics in CH3NH3PbBr3 and CH3NH3PbI3 Perovskite Films: Influence of Exciton Binding Energy, Journal of Physical Chemistry Letters 6, 4688 (2015).

[347] J. C. de Mello, H. F. Wittmann, and R. H. Friend, An improved experimental determination of external photoluminescence quantum efficiency, Advanced Materials 9, 230 (1997).

[348] A. R. Johnson, S.-J. Lee, J. Klein, and J. Kanicki, Absolute photoluminescence quantum efficiency measurement of light-emitting thin films, Review of Scientific Instruments 78, 096101 (2007).

[349] S. Leyre, E. Coutino-Gonzalez, J. J. Joos, J. Ryckaert, Y. Meuret, D. Poelman, P. F. Smet, G. Durinck, J. Hofkens, G. Deconinck, and P. Hanselaer, Absolute determination of photoluminescence quantum efficiency using an integrating sphere setup, Review of Scientific Instruments 85, 123115 (2014).

[350] W. Yang, Y. Yao, and C.-Q. Wu, Mechanism of charge recombination in meso-structured organic-inorganic hybrid perovskite solar cells: A macroscopic perspective, Journal of Applied Physics 117, 155504 (2015).

[351] H. C. Kwon, A. Kim, H. Lee, D. Lee, S. Jeong, and J. Moon, Parallelized Nanopillar Perovskites for Semitransparent Solar Cells Using an Anodized Aluminum Oxide Scaffold, Advanced Energy Materials 6, 1 (2016).
Summary

Optoelectronic devices have changed human life tremendously. Lighting, energy conversion and storage, communication and imaging are only a few examples of the applications that rely on optoelectronics. Further advances in low-cost, efficient devices requires investigating new materials and designs. Halide perovskites are a promising class of materials for incorporation in optoelectronics with higher efficiency and lower cost. The solution processability of these materials provides unique opportunities for simple nanostructure fabrication. Integration of micro and nanostructured perovskites will open up opportunities for approaching highly efficient devices. In this thesis we explore the fabrication and characterization of monocry stalline halide perovskite micro and nanostructures from solution.

Single crystals are the simplest form of a material and thus provide an ideal model system to study the most fundamental properties of the material in the absence of grain boundaries. Most previous work in this area involves perovskite single crystals grown using lengthy chemical methods, which yield large crystals that are far outside the range that is useful for most optoelectronic devices. In Chapter 2 we present a method based on confining the solvent evaporation to fabricate thin halide perovskite single crystals that still have lateral dimensions large enough to make microscale devices. The single crystallinity is confirmed by electron backscatter diffraction (EBSD). Simple back-contacted CH$_3$NH$_3$PbBr$_3$ single crystal devices are made by deposition of the crystals on pre-fabricated metal electrodes. These devices show photovoltaic behaviour, and present a platform to study the fundamental properties of single crystal perovskites in operando.

To have perovskite optoelectronic devices commercially available their working principle and mechanisms, especially the ones that have led to performance instability and degradation, should be fully understood. One of the main causes presented for the short and long-term instability is ionic migration. Halide perovskites as ionic semiconductors are not only electronic but also ionic conductors. In Chapter 3 we employ the back contacted CH$_3$NH$_3$PbBr$_3$ single crystal devices to study the ionic migration in the presence of applied electric field. The synchrotron-based nanoprobe X-ray fluorescence (nano-XRF) mapping with 250 nm resolution is used to quantify the changes of bromide distribution...
at the nanoscale under applied electric fields. By systematically manipulating
the halide concentration laterally with applied voltage bias we observe a quasi-
reversible field-assisted halide migration. The photoluminescence mapping of
the crystals under the same biasing conditions reveals the corresponding changes
due to halide migration in the optical quality of CH$_3$NH$_3$PbBr$_3$ single crystals.
Higher local bromide concentration is correlated with superior optoelectronic
performance in CH$_3$NH$_3$PbBr$_3$, while regions with lower bromide concentration
show decreased PL intensities. Density functional theory (DFT) computations
indicate that bromide ions experience a low energy barrier to migration when
the CH$_3$NH$_3^+$ ions are aligned in the presence of an electric field. In this scenario,
the migration of halide ions is expected to change the local stoichiometry and
therefore optoelectronic quality of perovskite devices during operation. This study
clarifies that halide migration is a challenge that is intrinsic to the absorber and one
that may play a determining role in the ultimate performance limits of perovskite
devices.

In Chapter 4 we present a method to fabricate free-standing solution-based vertical
perovskite nanowires. In this method, the perovskite solution is extruded out of the
pores of an anodized aluminum oxide (AAO) template by applying a pressure gra-
dient. Free-standing nanowire arrays are formed upon subsequent evaporation of
solvent during the annealing. Transmission electron microscopy (TEM) diffraction
confirms the single crystallinity along the nanowire length. The photolumines-
cence quantum yields (PLQY) of single perovskite nanowires measured using an
integrating sphere microscopy setup reach values up to $\sim$29%. This technique can
be generally used to form perovskite nanostructures with arbitrary dimensions and
cross-sectional shape because the exit profile of the template is subsequently trans-
lated into the final semiconductor geometry. The concept of the fabrication process
is very similar to macroscopic profile extrusion used extensively in the plastics in-
dustry, but now applied to a nanoscale optoelectronics material. The simplicity and
fast speed of this technique make it as a promising approach for the large-scale in-
dustrial fabrication of optoelectronic devices based on perovskite nanostructured
arrays.

Highly efficient perovskite nanostructured optoelectronic devices will depend crit-
ically on the density of defects at the surface and in the bulk. Passivating the surface
defects with metal oxide such as Al$_2$O$_3$ has been introduced as a common strategy
to decrease the charge carrier recombination at the surface of perovskites. In Chapter 5
we study the surface passivation effect of alumina on perovskite nanowires
embedded in AAO templates. A similar extrusion technique with shorter time of the
applied pressure gradient is used to fill the AAO pores with perovskite nanowires.
These perovskite/alumina nanowire arrays are used as a well-controlled platform
to study the charge carrier dynamics and effect of surface passivation with alumina.
A charge carrier lifetime of more than 20 ns is calculated from obtaining the recom-
bination rate coefficients. We develop a model to relate the charge carrier lifetimes
with the nanowire radii. Using this model, we extract a remarkably low surface
recombination velocity (SRV) of $37.2 \pm 20$ cm.s$^{-1}$ for the perovskite/alumina inter-
face which confirms the passivation role of alumina. Perovskite nanowire arrays in AAO templates have high potential for integration in highly efficient optoelectronic devices due to the ease of fabrication and excellent photophysical properties. Overall, this thesis provides an insight into new solution-processed methods for fabrication of high quality single crystalline halide perovskite micro- and nanostructures. The fabricated perovskite microcrystals and nanowires are used as simple model systems to study the fundamental properties of halide perovskites by asking questions such as: Which ions are moving in halide perovskites under electric field? How does ionic migration affect the optoelectronic properties of halide perovskites? What is the potential for improving the surface properties of halide perovskites by alumina passivation? The answers to these questions expands our understanding of halide perovskite nanostructures and their potentials and limitations for incorporation into future optoelectronic devices.
Samenvatting

Opto-elektronische apparaten hebben de wereld om ons heen zeer ingrijpend beïnvloed. Verlichting, energieconversie en -opslag, communicatie en beeldvorming (imaging) zijn slechts enkele voorbeelden van toepassingen van de opto-elektronica. Om de vooruitgang in nieuwe, betaalbare, opto-elektronische apparaten met een hoge efficiëntie verder te stimuleren, is onderzoek naar nieuwe materialen en ontwerpen noodzakelijk. Halogenide perovskieten zijn een veelbelovende familie van materialen voor de incorporatie in opto-elektronische apparatuur, met hogere efficiëntie, en lagere kosten. De mogelijkheid om deze materialen te verwerken vanuit de oplossing biedt unieke mogelijkheden voor eenvoudige fabricatie van nanostructures. Daarnaast zal integratie van micro- en nano-gestructureerde perovskieten mogelijkheden scheppen tot de fabricatie van zeer efficiënte apparaten met nieuwe toepassingen. Dit proefschrift richt zich op de fabricage, en karakterisatie, van deze monokristallijne, halogenide, perovskieten nanostructures, gefabriceerd vanuit de oplossing.

Monokristallen zijn de meest eenvoudige soort materiaal, en zijn daarom bij uitstek geschikt om als modelsysteem te dienen voor het bestuderen van fundamentele eigenschappen van het materiaal, zonder effecten van korrelgrenzen (grain boundaries) te ondervinden. Het meeste voorafgaande onderzoek op dit onderwerp heeft zich gericht op monokristalperovskieten, die volgens lange (en vaak gecompliceerde) chemische methodes zijn gesynthetiseerd, waarbij lange kristalstructuren ontstaan, die niet bruikbaar zijn voor de voornaamste toepassingen in opto-elektronische apparaten. In hoofdstuk 2 wordt een methode gepresenteerd waar door insluiten van vloeistofevaporatie dunne, halogenide, perovskieten monokristallen worden gefabriceerd, waarbij de laterale dimensies nog van een proportie zijn dat apparaten op microschaal kunnen worden verwezenlijkt. De monokristalliniteit wordt bevestigd met de elektronterugstrooidiffactietechniek (electron back-scatter diffraction, EBSD). Eenvoudige 'back-contact' zonnecellen op basis van CH₃NH₃PbBr₃ monokristallen zijn gemaakt door middel van depositie van deze kristallen op een netwerk van voorgefabriceerde metalen elektroden. Deze zonnecellen verdienen de naam, doordat zij fotovoltaïsch gedrag vertonen, en bieden daarmee een platform
Samenvatting

voor onderzoek naar de fundamentele eigenschappen van monokristallijne perovskieten, *in operando*.

Om de commercialisatie van opto-elektronische apparaten van perovskiet te realiseren, moeten de werkingsprincipes -en mechanismen volledig worden begrepen, met inbegrip van de stabiliteit- en degradatieprocessen, als grootste invloeden op de efficiëntie, en prestaties over tijd, van deze apparaten. Ionenmigratie is een van de voornaamste oorzaken voor korte- en lange termijn instabiliteit. Halogenide perovskieten zijn zowel elektronische -en ionische geleiders, als ionische halfgeleiders. In *hoofdstuk 3* worden de ‘back-contact’ CH$_3$NH$_3$PbBr$_3$ monokristallen apparaten gebruikt om ionenmigratie te bestuderen onder invloed van een aangebracht elektrisch veld. Nanosonde X-ray fluorescentie metingen, gedaan in een synchrotron, worden gebruikt om een afbeelding met een resolutie van 250 nm te realiseren, om de veranderingen in bromidedistributie op de nanoschaal in kaart te brengen, onder invloed van een aangebracht elektrisch veld. Door systematisch de halogenideconcentratie lateraal aan te passen, door middel van een toegepaste voorspanning, wordt een quasi-reversibele, halogenide migratie gerealiseerd. De fotoluminescentie -afbeelding van de kristallen onder dezelfde toegepaste voorspanning toont de overeenstemmende veranderingen in de optische kwaliteit van de CH$_3$NH$_3$PbBr$_3$ monokristallen, ten gevolge van de halogenide migratie. Een hogere, plaatselijke, concentratie van bromide is gecorreleerd met superieure opto-elektronische prestaties, terwijl regio’s met lagere bromide concentraties verlaagde fotoluminescentie-intensiteiten vertonen. Dichtheidsfunctionaal-theorieberekeningen (density function theory, DFT) bepalen dat bromide-ionen een lage energiebarrière ondervinden voor migratie, wanneer de CH$_3$NH$_3^+$ ionen worden gealigneerd door aanbrenging van een elektrisch veld. In dit scenario is de verwachting dat de migratie van halogenide ionen verandert door de plaatselijke stoichiometrie, en daarbij de opto-elektronische kwaliteit van de perovskietenapparaten tijdens gebruik. Deze studie verduidelijkt dat de halogenidenmigratie een uitdaging is, die intrinsiek is aan het absorberend materiaal, en een bepalende rol kan spelen in de uiteindelijke prestatielimieten van perovskieten apparaten.

In *hoofdstuk 4* wordt een methode gepresenteerd om perovskieten verticaal-vrijstaande nanodraden te fabriceren, vanuit de oplossingsfase. In deze methode worden de perovskieten in oplossingsfase uit een sjabloon met geanodiseerde aluminiumoxide (AAO) poriën geëxtrudeerd, door toepassing van een drukgradient. Reeksen van vrijstaande nanodraden worden gevormd door herhaalde evaporatie van de oplossing, tijdens thermisch gloeien. Transmissie-elektronenmicroscopiediffraactie bevestigt de monokristalliniteit van de nanodraden over hun gehele lengte. De fotoluminescentiekwantumopbrengsten (photoluminescence quantum yields, PLQY) van monokristallen perovskieten nanodraden, gemeten met behulp van een bol van Ulbricht microscoop, behalen waardes tot 29%. Deze techniek kan algemeen gebruikt worden om perovskieten nanostructuren te fabriceren met willekeurige dimensies en arbitraire transversale vorm, doordat het uitgangsprofiel van het sjabloon leidend is in de uiteindelijke geometrie van de vorm, die het halfgeleidermateriaal aanneemt. Het concept van
Samenvatting

het fabricatieproces heeft grote gelijkenis met macroscopische sjabloonextrusie, zoals extensief gebruikt wordt in de plasticindustrie, maar nu toegepast op een opto-elektronisch materiaal op nanoschaal. De eenvoud en snelheid van deze methode maken dat het een veelbelovende methode is voor fabricatie van opto-elektronische apparaten op industriële schaal, gebaseerd op perovskieten nanogestructureerde reeksen en matrices.

Perovskieten nanogestructureerde opto-elektronische apparaten met hoge efficiëntie zijn sterk afhankelijk van de mate en dichtheid van deficiënties in het kristalrooster, zowel aan het oppervlak alsmede in de bulk van het materiaal. Oppervlaktepassivering met metaaloxide, zoals Al$_2$O$_3$, is een welbekende strategie om ladingdragerrecombinatie aan het oppervlak van perovskietstructuren tegen te gaan. In hoofdstuk 5 wordt het oppervlaktepassiveringseffect van aluminiumoxide op perovskieten nanodraden, ingebed in AAO sjablonen, bestudeerd. Een vergelijkbare extrusietechniek wordt gebruikt om de AAO-poriën te vullen met perovskieten nanodraden, waarin voor een kortere tijd een drukgraadiënt wordt aangebracht. Deze reeksen van perovskiet-aluminiumoxide nanodraden worden gebruikt als een po- dium om goed controleerbaar de ladingdragerdynamiek te bestuderen, alsmede de uitwerking van oppervlaktepassivering met aluminiumoxide. Een ladingsdragerlevensduur van meer dan 20 ns wordt aangetoond, door middel van het verkrij- gen van recombinitiestoelsnemendeficiënten, door fotoluminescentieversporen aan te passen aan een reactiesnelheidsmodel (rate equation model). De ladingsdragerlevensduur kan worden bepaald met behulp van informatie over de radii van de nanodraden, door middel van een zelfontwikkeld model. Met hetzelfde model wordt een opmerkelijk lage oppervlakterecombinitiesnelheid (surface recombina- tion velocity, SRV) van 37.2 ±20 cm/s bepaald voor het perovskiet-aluminiumoxide raakvlak, hetgeen de passiveringsrol van aluminiumoxide bevestigt. Perovskieten nanodraadreeksen in AAO sjablonen hebben een grote potentie voor integratie in opto-elektronische apparaten met hoge efficiëntie, doordat ze relatief makkelijk te fabriceren zijn, en excellente fotofysische eigenschappen vertonen.

Samenvattend biedt dit proefstuk inzicht in nieuwe technieken om uit de oplossingsfase verwerkte, hoge kwaliteit, monokristallijne, halogenide, perovs- kieten, micro- en nanostructuren te fabriceren. De gefabriceerde perovskieten microkristallen en nanodraden worden gebruikt als eenvoudige modelsystemen om de fundamentele eigenschappen van halogenide perovskieten te bestuderen, door vragen te stellen zoals: "Welke ionen migreren in halogenide perovskieten onder het aanbrengen van een elektrisch veld", "Hoe beïnvloedt ionenmigratie de opto-elektronische eigenschappen van halogenide perovskieten", en "Wat is de verbeterpotentie van oppervlakte-eigenschappen van halogenide perovskieten, met gebruik van aluminiumoxide-oppervlaktepassivering?"De antwoorden op deze vragen verbreden ons begrip van halogenide, perovskieten nanosucturen, en de potenties en limitaties voor de incorporatie van deze materialen in toekomstige opto-elektronische apparaten.
List of publications

This thesis is based on the following publications:

• *Growth and characterization of PDMS-stamped halide perovskite single microcrystals*
  P. Khoram, S. Brittman, W.I. Dzik, J.N.H. Reek, E.C. Garnett
  J. Phys. Chem. C, 2016, 120 (12), 6475. *(Chapter 2)*

• *Direct observation of halide migration and its effect on the photoluminescence of methylammonium lead bromide perovskite single crystals*
  Y. Lou*, P. Khoram*, S. Brittman, Z. Zhu, B. Lai, S.P. Ong, E.C. Garnett, D. Fenning
  Adv. Mater., 2017, 29 (43), 1521. *(Chapter 3)*
  *equal contribution

• *Perovskite nanowire extrusion*
  S.Z. Oener*, P. Khoram*, S. Brittman, S.A. Mann, Q. Zhang, Z. Fan, S.W. Boettcher, E.C. Garnett
  Nano Lett., 2017, 17 (11), 6557. *(Chapter 4)*
  *equal contribution

• *Charge carrier dynamics at the perovskite/alumina interface*
  P. Khoram, S.Z. Oener, E.C. Garnett
  (in preparation) *(Chapter 5)*
List of publications

Other publications by the author:

- *Organic ternary solar cells: A review*
  T. Ameri, P. Khoram, J. Min, C.J. Brabec
  Adv. Mater., 2013, 25 (31), 1521.

- *Morphology analysis of near IR sensitized polymer/fullerene organic solar cells by implementing low bandgap heteroanalogue C-/Si-PCPDTBT*
  T. Ameri, P. Khoram, T. Heumuller, D. Baran, E. Machui, A. Troeger, V. Sgobba, D.M. Guldi, M. Halik, S. Rathgeber, U. Scherf, C.J. Brabec
  J. Mater. Chem. A., 2014, 2 (45), 19461.
Acknowledgements

It was more than four years ago when I put my first step into Amolf, a green building which became my second home during the last years. At that moment I could not imagine the great adventure I was going to have ahead, which one of its results is this thesis. The significant impact of these years in my life is beyond this book, and here I would like to express my gratitude to all of those who directly and indirectly have contributed.

First of all, I would like to thank my supervisor, Erik Garnett, for giving me the opportunity to start this journey and do my PhD in his group. Erik is a great scientist that teaches his knowledge unconditionally to his students. He showed me that not only a good and truthful science matters, but also being creative is necessary to do successful research. Having a supervisor who can not be convinced easily taught me how to become truly persistent, as himself is. Erik, I am grateful for the invaluable support and feedbacks you provided, and your openness for discussing anything. I learned from you to be stubborn in research, not to give up and get disappointed by the failures too soon, and to look for a clever and creative solution to the challenges on our way. Then I would like to acknowledge the support from my co-promoter Albert Polman, thank you for providing a collaborative culture and supportive atmosphere not only at LMPV and nanophotonic department, but also for the whole Amolf.

A couple of months after I started at Amolf, a postdoc researcher joined our group whose presence changed my vision and ultimate goal entirely. Sarah, without you this work would not ended up as it is today, thank you for all the scientific knowledge and manners you taught me. Your humbleness showed me that it is not about who is doing the science, but the science itself. Your organized and calm way to approach the challenges, always stays as an example to me. I have very deep respect for you, and I learned much more from you than I can express here in a few lines.

Doing scientific work without cooperation and interaction of people is not possible. During my PhD I had the chance to do research with collaborators whom provided invaluable learning and team work opportunities. I would like to thank David Fenning and Grace Lou for the work that ended up as the third chapter of this thesis. David, thank you for giving insightful feedbacks and being supportive through the
Acknowledgements

project which did not seem easy at the beginning. Grace, thank you for the very
active cooperation and all the useful discussions on this project. Sarah, also thank
you for accepting to go and do the experiments in Argonne National Lab on behalf
of me, despite the very short notice, when it turned out that it was impossible for
me to go.

I would like to thank all the members of Nanoscale solar cells group for their con-
tribution, and also for making a pleasant working atmosphere. Sebastian, thanks
for the collaboration in the perovskite nanowire project. That was one of the most
fun, and most efficient projects I have ever done. It would have not been possible to
make the "pasta wires" without your creative contribution, and openly helping me.
Sander, thanks for your training on integrating sphere setup, and all the insights
to understand the theory behind. Also thanks for teaching me about directivity,
escape probability and FDTD simulation. I did not continue on that project, but all
I learned stayed useful. I would like to thank the members of our little perovskite
team: Gede, Shanti, Haralds, Teo and Forrest, for all the discussions, meetings and
projects. Niels, I would like to especially thank you for translating of the summary
of this thesis to Dutch, and Julia thanks for re-checking it. Michiel, I always remember
the first day that we started together and thank you for all the moments of fun
and sports! And, thanks to the rest of current and former members of the group:
Beniamino, Biplab, Eric, Harshal, Hongyu, Jia, Lai-Hung, Cristina, Mohamed, Jenny
and Sven, for all the valuable discussions, and also fun moments.

This experimental work would have not been possible without the incredible and
easy-to-reach support provided by the technicians. I would like to express my deep
appreciation to all the support staff at Amolf. Henk-Jan, thank you for your wonder-
ful graphic designs, including the first figure of this thesis and also the cover design
for our paper. I’m also very grateful for your support during my writing phase (Also
thanks Merel!) and your friendship which I hope it will continue. Marc, thank you
for being the great technician of our group. Definitely without your always available
support, none of us could do our research as smoothly and conveniently as we do
today in the lab. Thanks for all the help with maintaining the dirty glovebox (and
also all other equipment and chemicals), I still remember that night that you came
at 12 a.m. for regenerating the glovebox! Dirk-Jan, thanks for your help with the
schematics of my first and second papers. Jan, thanks for providing the electrical
engineering support for our group. Thank you for training us on ESD, and helping
with handling my very sensitive samples! Clyde, thanks for the fantastic facility
support you provide. Your cheerful manner makes this building a better place
to be. Hans, Dimitry, Andries and Bob, what you are doing at the nanocenter is
simply amazing! Thanks for always coming up with a smart solution for fabricating
complex structures, for keeping the clean room pleasant, and for patiently training
and taking care of the equipments. Dion and Niels, thank you for your quick helps
with my orders, which almost always happened to be last minute!

Our group is part of the program of Light management for Photovoltaics (LMPV).
I would like to thank the group leaders: Albert Polman, Bruno Ehrler and Esther
Alarcon Llado for organizing the meetings, symposia and outings, and also for the
Acknowledgements

high quality discussions and feedback. Thanks also to the LMPV group members, especially: Verena, Andrea, Mark Knight, Piero, Tianyi, Moritz, Benjamin (and especially thanks for the help in TCSPC setup), Lucie, Loreta, Christian, Nasim and Mark Aarts, for providing a collaborative atmosphere. Apart from LPMV, we are also part of nanophotonic department at Amolf, with weekly nanophotonic colloquia and poster sessions which provides an open and active atmosphere for learning, discussion and receiving feedbacks. I would like to thank the group leaders: Femius Koenderink, Ewold Verhagen and Said Rodriguez, and all the current and previous group members, especially: Sophie, Nick, Magda, Benjamin, Freek, Rick, Clara, Lutz, Annemarie, Kevin, Hugo, Isabelle, Ruslan, Christiana, John, Juha, Robin, Giada, Nikhil, and Lorentzo. Thank you for making the working place pleasant, and all the good moments out of work.

Being at Amolf gave me the chance of having invaluable friendships which stays with me the rest of my life. My science girls: Agata, Cristina, Jenny and Giada, making our little gang was one of the best things happened to me in the past few years. I hope your company and friendship stays as a life lasting thing, and we repeat our adventurous travels and chillin home-stays together over and over again. Cristina, you are my first friend in Amsterdam, someone I know I can always count on her wisdom, and I was so lucky to share a lot of intimate moments with you. I am so happy you accepted to be my paranymph, thanks a lot! Tzeni, my dear neighbor, officemate, colleague and friend, I am so happy that I could have the chance of knowing you and sharing a lot of moments with you. Your golden heart shines wherever you go. Thanks for tolerating me on my talkative moods at the office, and for all the energetic chitchats and generous hugs. Also thank you for being my paranymph! Agata, you are one of those persons I always feel proud of having their friendship. Your strong character always spread good vibe around, thank you for your support and encouragement in hard moments. Giada, thanks for all the good moments and the hugs, exactly whenever needed!

In these years of living in Amsterdam a few people made it even more feels like home, with having the pleasure of talking in Persian and having the same roots. Parisa, you were the first Iranian I met here, and I am so happy that our friendship lasts so long. Thanks for all the long nights, good moments and your support in hard ones. Payam, I’m so grateful for having the opportunity to know you, and having a Mashhadi friend in this town! Thanks to you and Kim for having your door always open for me. Whenever something really bad happened in these years, I knew where is the first place I can go! I am also delighted that I had a few Iranian colleagues. Fatemeh and Abbas, thanks for your welcoming and support when I just started. Nasim, thanks for all the scientific and non-scientific deep conversations I could have with you. I feel very lucky of having your friendship with such a positive vibe. It was a pleasant luxury for me to have a few of my cousins living in the same country: Sohrab, Marjaneh, Amirali and Saeideh, thank you for giving me the feeling of family during these years of being in the Netherlands.

I would like to thank all of those Amolfers whom we did not share much scientific collaborations, but the times we had together made the quality of these years much
Acknowledgements

higher: Federica, Yuval, Marco, Lukas, Hans, Iarik (also thanks for the preparation of precursors!), Augustin, Giorgio, Mathijs, Jacopo, Olga, Nicola, Mario, Michele, Giulia, Oleg, Aditya, Roberto (and also Katya), Alessandro, Simone, and Noreen. My office-mates: Amy, Jenny and (the regular visitor) Sven, thank you for the daily fun conversations, and for tolerating me during the writing phase, I know I was not very pleasant those days! I would also like to thank my climbing partners: Soraya and Maureen, thank you girls for those sportive and joyful moments. And my deep gratitude goes for my amazing friends, near or far, those who had a big impact on me, and were always cheerfully supportive: Juli, Alberto, Anastasia, Farbod, Farzaneh, Taees, Mona, Pardis, Parisa, and Negar.

When I was doing my master in Germany, I was very fortunate to have a very strong woman as my supervisor, someone who encouraged me to do PhD, and always remains as an example for me. Tayebeh, thank you for teaching me many things about science, research and life!

Moni and Laci, I am very thankful for your support and great hospitality, especially during our writing phase. It was tough but your kindness made it much easier to go through. Nagyon köszönöm szépen!

One of the most precious things that happened to me during these years was meeting you, Abel. Thank you for your endless care and love, for believing in me, and for all the fabulous moments that gave me energy to keep moving forward. Without you this work would have not been ended like this, and I am so excited to continue to the next adventurous steps with you!

Finally I would like to thank my beloved parents, Mitra and Masoud, and my little sister, Taraneh. Tari, I am so grateful for having the best sister in the world, someone I can always rely on, and the one who understands me the most! Thank you so much for the great support during my PhD, and especially for designing the cover of this thesis! Who and where I am today would not be in this way without the unconditional love and support of my parents. I would like to end this part by saying a few words to them:

ماً، و في رمز عزيزه، از حمايت ها و عشق بي دريغ شما، بسيار سياستگازارم. بدون شما، هرگز به اينجا نمي رسيم و تا هميشه برای داشتن شما قادرانم.