



HAL
open science

Halide Perovskites: Low Dimensions for Devices

Edoardo Ruggeri, Samuel D Stranks, Emmanouil Manidakis, Constantinos C Stoumpos, Claudine Katan

► **To cite this version:**

Edoardo Ruggeri, Samuel D Stranks, Emmanouil Manidakis, Constantinos C Stoumpos, Claudine Katan. Halide Perovskites: Low Dimensions for Devices. ACS Energy Letters, 2019, 4 (12), pp.2902-2904. <10.1021/ac-senergylett.9b02263>. <hal-02360410>

HAL Id: hal-02360410

<https://hal.science/hal-02360410v1>

Submitted on 11 Dec 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

Halide Perovskites: Low Dimensions for Devices

Edoardo Ruggeri,^a Samuel D. Stranks,^{a,b} Emmanouil Manidakis,^c Constantinos C. Stoumpos,^{*,c} Claudine Katan^{*,d}

^aCavendish Laboratory, University of Cambridge, JJ Thomson Avenue, CB3 0HE, Cambridge, United Kingdom

^bDepartment of Chemical Engineering & Biotechnology, University of Cambridge, Philippa Fawcett Drive, Cambridge CB3 0AS, United Kingdom

^cDepartment of Materials Science and Technology, Voutes Campus, University of Crete, Heraklion GR-70013, Greece

^dUniv Rennes, CNRS, ISCR - UMR 6226, Rennes F-35000, France

Celebrating 10 years from the technological revolution brought about by the first report of halide perovskite solar cells, *Symposium G* of the *EMRS Spring Meeting 2019* was dedicated to the memory of the late George C. Papavassiliou (Figure 1), a vibrant pioneer in the early days of the field during the 1990s. The Symposium, entitled “*Halide Perovskites: low dimensions for devices*”, to reflect the important potential of these tunable semiconductors in technology, was designed with the intention of bringing together researchers from across all breadths and lengths of the field. From the discovery of new materials to the study of their photophysical properties - from both theory and experiment viewpoints- to more technical studies related to the implementation of perovskites into functional devices, the Symposium highlighted most aspects of the perovskite research that have been actively studied to date. In this respect, the symposium proved successful in providing key opportunities for discussions on progress in new material development as well as to introduce new potential applications beyond optoelectronics, with energy-related developments standing out.



Figure 1. Photo of the late George Papavassiliou. (Photo courtesy of I. Koutselas.)

Among the 12 invited talks the 56 oral presentations and its 38 poster presentations (including a joint session with *Symposium B - Emerging photovoltaics: strategies for more stable devices*), the Symposium delivered lively discussion stimulated by the invited researchers who delineated the different themes of the Symposium. B. Lounis showed how the exciton-phonon coupling operates in perovskites, presenting an excellent account on the photo-physics of halide perovskite nanocrystals at the single-particle level¹. On a more applied topic, M. Bodnarchuk explained the intricacies of the synthesis and emission tuning of colloidal perovskite nanocrystals, showing how much the interface interactions between the inorganic perovskite and the organic surfactants can influence the properties, and proposed innovative methodologies on how to control the interactions². On the “phonon problem”, R. Schaller presented a “high-throughput” study of many perovskite derivatives, experimentally pinpointing the anharmonic nature of the phonons that derive from the dynamically disordered nature of the crystal lattice³. P. Plochocka covered the excitons present in the perovskites and highlighted very vividly how to manipulate excitons using (enormous) magnetic fields and extract useful information on their binding energy and lifetimes within the perovskite structure⁴. Shifting the dimensionality to perovskite nanowires, the presentation of E. Horvath introduced many innovative methods to produce functional perovskite nanowires that can be shaped “at will” to various morphologies, by manipulating the substrate pattern and the surface conditions⁵.

Two-dimensional (2D) halide perovskites, arguably one of the “hottest” topics in recent years, also had a strong representation with many talks on the topic from young investigators. The senior scientists were represented by S. Jin who explained how it is possible to construct heterostructures of these 2D materials akin to the development of III-V semiconductor heterostructures⁶. In addition, D. Mitzi -- a living legend in the halide perovskite field having almost single-handedly established the field in the 90’s and the 00’s - presented an excellent account on the historical evolution of the materials and explained where the field stands today⁷. C. Quarti (Figure 2) stimulated 2D perovskite discussions from the theory point of view, explaining what can be learned from modelling the optical properties of the materials and how polarons play a key role in the evolution of the physical properties of dimensionally reduced perovskites⁸.

The more traditional three-dimensional (3D) perovskites also had their key place in the Symposium, with their theoretical properties addressed as much as their different synthesis approaches, collectively revealing new permutations of the “malleable” perovskite structure. In an innovative and uncompromising presentation, A. Zunger cast a fresh eye on the halide perovskite structures - reframing them in the context of the polymorphous structure - to account for their unconventional features that are not easily addressable by means of conventional band structure calculations⁹. H. Hillebrecht gave an excellent solid-state synthesis “tutorial”, illustrating that the solid-state chemistry of halide perovskites is indeed very rich and well worth exploring further¹⁰. As he showed through a variety of crystal structures - from 3D “hollow” perovskites to 2D perovskites and molecular coordination compounds -- it is possible to find almost anything in a beaker of a stirred perovskite solution! Combining theory and experiment, G. Volonakis (Figure 2) achieved a remarkable feat: he was able to predict *in silico* and isolate *in vitro* a new member of the double perovskite family, which even more impressively possessed the optical properties predicted by theory¹¹.

On the perovskite device front, the Symposium (jointly with *Symposium B*) featured talks on the major debate revolving around halide perovskites, namely their long-term stability and viability. A. Mohite (Figure 3) presented recent progress in 2D perovskite solar cells explaining in great detail how parameters such as phase purity and crystallinity play important roles in the performance and stability of devices¹². A. Petrozza (Figure 3) focused on the intrinsic (in)stability of the perovskites governed by ionic motion and dynamic disorder within the materials, and on the unusual defect physics that are so important to the operation of perovskite photovoltaic devices¹³.

The Symposium of course featured a large number of young “rising stars” from the graduate school level all the way to senior postdoctoral researchers, all of whom contributed to advancing the scientific level of the symposium and moving perovskite systems a small but significant step forward. The covered topics ranging from the fundamental understanding of these remarkable materials to assessing their potential as a viable technology in the near future. In recognition of the prowess of the young investigators, awards were presented for the best graduate student (*EMRS Graduate Student Award*), awarded to Mr Young-Kwang Jung for his work on elucidating the green luminescence in the 0D perovskite Cs₄PbBr₆¹⁴. The best oral and best poster awards, sponsored by *Nature Materials*, were respectively awarded to Dr. Azhar Fakharuddin (Figure 2) for his talk on light-emitting diodes of two dimensional quasi-2D perovskites¹⁵



Figure II. Photo of the best oral winner (W), prize committee members (M), and Symposium G “Halide Perovskites: Low Dimensions for Devices” organizers (O) at the occasion of the E-MRS19 Spring Meeting. From left to right: Claudio Quarti (M), Claudine Katan (O), Jovana Milic (M), George Volonakis (M), Azhar Fakharuddin (W), and Constantinos Stoumpos (O). Absent from the picture: Samuel Stranks (O). (Photo courtesy of J. Even.)

and Géraud Delpont (Figure 3) for his poster discussing the diffusion of carriers in perovskite crystals via time-resolved photoluminescence microscopy¹⁶.

In the organizers’ view, as well as in the opinion of many participants, *Halide Perovskites: low dimensions*



for devices was a fruitful meeting with discussions and debates from all around the halide perovskite and many useful energy-related scientific conclusions reached. We believe that meetings with a similar scope should be held in the near future, since they will be beneficial for the advancement of the field – providing the critical links between fundamental science and applied device deployment.

Figure III. Photo of the best poster winner (W) and prize committee members (M) of Symposium G “Halide Perovskites: Low Dimensions for Devices” at the occasion of the E-MRS19 Spring Meeting. From left to right: Annamaria Petrozza (M), Aditya Mohite (M), and Géraud Delport (W). Absent from the picture: Richard Schaller (M). (Photo courtesy of J. Even)

AUTHOR INFORMATION

Corresponding Authors

*E-mail:

cstoumpos@materials.uoc.gr (C.C.S.).

*E-mail: claudine.katan@univ-rennes1.fr (C.K.).

Notes

Views expressed in this Energy Focus are those of the authors and not necessarily the views of the ACS. The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Symposium G of the 2019 E-MRS Spring Meeting was co-organized by Constantinos Stoumpos, Samuel Stranks and Claudine Katan. Emmanouil Manidakis and Edoardo Ruggeri were assistants of the symposium. The organizers acknowledge support from ACS Energy Letters, Nature Materials, M. Braun Inertgas-Systeme GmbH, Edinburgh Instruments Ltd and CNRS think tank GDR HPERO (<http://gdr-hpero.cnrs.fr/>). Catherine Kocher and Sylvain Schoeffter are gratefully acknowledged for their invaluable logistical support.

References

- (1) Tamarat, P.; Bodnarchuk, M. I.; Trebbia, J. B.; Erni, R.; Kovalenko, M. V.; Even, J.; Lounis, B. The Ground Exciton State of Formamidinium Lead Bromide Perovskite Nanocrystals Is a Singlet Dark State. *Nat. Mater.* **2019**. <https://doi.org/10.1038/s41563-019-0364-x>.
- (2) Bodnarchuk, M. I.; Boehme, S. C.; Ten Brinck, S.; Bernasconi, C.; Shynkarenko, Y.; Krieg, F.; Widmer, R.; Aeschlimann, B.; Günther, D.; Kovalenko, M. V.; et al. Rationalizing and Controlling the Surface Structure and Electronic Passivation of Cesium Lead Halide Nanocrystals. *ACS Energy Lett.* **2019**. <https://doi.org/10.1021/acsenenergylett.8b01669>.
- (3) Guo, P.; Mannodi-Kanakkithodi, A.; Gong, J.; Xia, Y.; Stoumpos, C. C.; Cao, D. H.; Diroll, B. T.; Ketterson, J. B.; Wiederrecht, G. P.; Xu, T.; et al. Infrared-Pump Electronic-Probe of Methylammonium Lead Iodide Reveals Electronically Decoupled Organic and Inorganic Sublattices. *Nat. Commun.* **2019**. <https://doi.org/10.1038/s41467-019-08363-2>.
- (4) Baranowski, M.; Zelewski, S. J.; Kepenekian, M.; Traoré, B.; Urban, J. M.; Surrente, A.; Galkowski, K.; Maude, D. K.; Kuc, A.; Booker, E. P.; et al. Phase-Transition-Induced Carrier Mass Enhancement in 2D Ruddlesden–Popper Perovskites. *ACS Energy Lett.* **2019**. <https://doi.org/10.1021/acsenenergylett.9b01435>.
- (5) Ćirić, L.; Ashby, K.; Abadie, T.; Spina, M.; Duchamp, M.; Náfrádi, B.; Kollár, M.; Forró, L.; Horváth, E. Mechanical Response of $\text{CH}_3\text{NH}_3\text{PbI}_3$ Nanowires. *Appl. Phys. Lett.* **2018**. <https://doi.org/10.1063/1.5023115>.
- (6) Fu, Y.; Hautzinger, M. P.; Luo, Z.; Wang, F.; Pan, D.; Aristov, M. M.; Guzei, I. A.; Pan, A.; Zhu, X.; Jin, S. Incorporating Large A Cations into Lead Iodide Perovskite Cages: Relaxed

- Goldschmidt Tolerance Factor and Impact on Exciton–Phonon Interaction. *ACS Cent. Sci.* **2019**. <https://doi.org/10.1021/acscentsci.9b00367>.
- (7) B. Mitzi, D. Introduction: Perovskites. *Chem. Rev.* **2019**. <https://doi.org/10.1021/acs.chemrev.8b00800>.
- (8) Thouin, F.; Valverde-Chávez, D. A.; Quarti, C.; Cortecchia, D.; Bargigia, I.; Beljonne, D.; Petrozza, A.; Silva, C.; Srimath Kandada, A. R. Phonon Coherences Reveal the Polaronic Character of Excitons in Two-Dimensional Lead Halide Perovskites. *Nat. Mater.* **2019**. <https://doi.org/10.1038/s41563-018-0262-7>.
- (9) Zhao, X.; Dalpian, G. M.; Wang, Z.; Zunger, A. The Polymorphous Nature of Cubic Halide Perovskites. *arXiv:1905.09141v1*. **2019**.
- (10) Daub, M.; Hillebrecht, H. First Representatives of (210)-Oriented Perovskite Variants – Synthesis, Crystal Structures and Properties of the New 2D Hybrid Perovskites A[HC(NH₂)₂]PbI₄; A=[C(NH₂)₃],[HSC(NH₂)₂]. *Zeitschrift für Krist. - Cryst. Mater.* **2018**, 233 (8), 555–564.
- (11) Volonakis, G.; Sakai, N.; Snaith, H. J.; Giustino, F. Oxide Analogs of Halide Perovskites and the New Semiconductor Ba₂AgIO₆. *J. Phys. Chem. Lett.* **2019**. <https://doi.org/10.1021/acs.jpcclett.9b00193>.
- (12) Tsai, H.; Asadpour, R.; Blancon, J. C.; Stoumpos, C. C.; Durand, O.; Strzalka, J. W.; Chen, B.; Verduzco, R.; Ajayan, P. M.; Tretiak, S.; et al. Light-Induced Lattice Expansion Leads to High-Efficiency Perovskite Solar Cells. *Science*. **2018**. <https://doi.org/10.1126/science.aap8671>.
- (13) Motti, S. G.; Meggiolaro, D.; Barker, A. J.; Mosconi, E.; Perini, C. A. R.; Ball, J. M.; Gandini, M.; Kim, M.; De Angelis, F.; Petrozza, A. Controlling Competing Photochemical Reactions Stabilizes Perovskite Solar Cells. *Nat. Photonics* **2019**. <https://doi.org/10.1038/s41566-019-0435-1>.
- (14) Jung, Y.-K.; Calbo, J.; Park, J.-S.; Whalley, L. D.; Kim, S.; Walsh, A. Intrinsic Doping Limit and Defect-Assisted Luminescence in Cs₄PbBr₆. *J. Mater. Chem. A* **2019**. <https://doi.org/10.1039/c9ta06874k>.
- (15) Fakharuddin, A.; Qiu, W.; Croes, G.; Devižis, A.; Gegevičius, R.; Vakhnin, A.; Rolin, C.; Genoe, J.; Gehlhaar, R.; Kadashchuk, A.; et al. Reduced Efficiency Roll-Off and Improved Stability of Mixed 2D/3D Perovskite Light Emitting Diodes by Balancing Charge Injection. *Adv. Funct. Mater.* **2019**. <https://doi.org/10.1002/adfm.201904101>.
- (16) Stavrakas, C.; Delport, G.; Zhumekenov, A. A.; Anaya, M.; Chahbazian, R.; Bakr, O. M.; Barnard, E. S.; Stranks, S. D. Visualizing Buried Local Carrier Diffusion in Halide Perovskite Crystals via Two-Photon Microscopy. *arXiv:1909.13110v1*. **2019**.