Poster

Hybrid materials of metal halide nano-sized clusters orderly confined in single crystal metal-organic reticular materials

O. Hordiichuk[1,2], Y. Okis[1,2], A. Kuznietsov[1,2], A. Yanchak[1,2], J. de Montmollin[1,2], C. Fuller[3], M. Wörle[1], D. Chernyshov[3], M. Kovalenko[1,2]

[1]Laboratory of Inorganic Chemistry, Department of Chemistry and Applied Biosciences, ETH Zürich, Zürich, Switzerland, [2]Laboratory for Thin Films and Photovoltaics, Empa—Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland, [3]Swiss-Norwegian Beamlines, ESRF, Grenoble, France

holeh@ethz.ch

Constraining spatial dimensionality of electronically extended systems by tailoring crystal structure, size and shape of inorganic compounds at nanoscale often endows the resulting materials with extraordinary optoelectronic, magnetic and catalytic properties [1, 2]. A recent prominence of inorganic and hybrid – organic-inorganic – lead halide three- and two-dimensional perovskites as exceptional materials for optoelectronic applications has stimulated studies of other metal halide compounds leading to discoveries of materials with diverse and novel functionalities [2-5]. We envisioned an extension of the structural space accessible for metal halides, in terms of atomic connectivity and electronic dimensionality, by utilising crystalline porous templates as hosts for metal halides crystallization. Atomically defined periodically ordered metal halide nano-sized clusters and their properties can thus be engineered well beyond the structural motives known from the conventional free-space crystallization.

We have achieved successful results with metal-organic frameworks and polyhedra as the templates and various main-group and transition metal halides, having obtained unique nano-sized clusters within the pores. We demonstrate the possibility of obtaining different structures by changing parameters of the reticular templates and crystallization conditions. The structures were determined with atomic resolution using single-crystal X-ray diffraction methods. In the cases of partial occupancy of the pores by clusters, the pronounced structured X-ray diffuse scattering revealed presence of short-range correlations between empty and occupied cavities. We managed to characterize the local structures using a recently developed deep learning method by treating the systems as a substitutional disorder and factorizing the diffuse scattering intensities into form-factor and short-range correlation components [6]. Characterization and synthetic control of arrangement of such optically active clusters on a local scale opens opportunities to study and engineer collective phenomena. We anticipate that such confined molecularly templated crystallization will evolve into an attractive materials design strategy.

[1] Gonzalez, M. I., Turkiewicz, A. B., Darago, L. E., *et al*. (2020). *Nature*, **577**, 64–68.

[2] Kovalenko M. V., Protesescu L., Bodnarchuk M. I. (2017). *Science*, **358** (6364), 745–750.

[3] Yakunin S., Benin B. M., Shynkarenko Y., *et al.* (2019). *Nature Materials*, **18**, 846–852.

[4] McCall K. M., Morad V., Benin B. M., Kovalenko M. V. (2020). *ACS Materials Lett*. **2** (9), 1218–1232.

[5] Morad V., Shynkarenko Y., Yakunin S., *et al*. (2019). *J. Am. Chem. Soc.*, **141**, 9764–9768.

[6] Fuller, C. A. & Rudden, L. S. P. (2024). *IUCrJ*, **11**, 34-44.