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promote the hydrogenation of the C=C bond to the furan ring while the metallic Ni sites are involved in the ring-opening hydrogenolysis of the C–O bond of the tetrahedron furan ring.

Furthermore, Li and co-workers have indeed demonstrated that the strategy involving carbonylation and the tandem hydrogenation is a general task that can be applied to a variety of substrates: for example, 5-HMF can be efficiently used for preparing hydroxylalkanoates with a seven-carbon chain. At the same time, the research group has demonstrated how 0.93 g of 6-HMC can be prepared from 1 g of hemicellulose. In particular, the acid hydrolysis reaction allows hemicellulose to be converted into FUR in high yield (95%), the resulting FUR to be selectively hydrogenated by means of a Cu-based catalyst into FAL, and then for FAL to be transformed into 6-HMC by means of the above-described one-pot carbonylation-hydrogenation process.

In conclusion, the work of Li and co-workers presents an elegant and solid combination of homogeneous and heterogeneous catalytic processes—one devoted to the carbonylation of the FUR alcohol to MFA and the other enabling the hydrogenolysis of MFA into 6-HMC—paving the way for the production of biodegradable plastics from renewable lignocellulosic biomasses.¹⁰

DECLARATION OF INTERESTS

The authors declare no competing interests

1. Rosenboom, J.-G., Langer, R., and Traverso, G. (2022). Bioplastics for a circular economy. *Nat. Rev. Mater.* 7, 1–21.
2. Brodin, M., Vallejos, M., Tanase Opedala, M., Area, M.C., and Chinga-Carrasco, G. (2017). Lignocellulosics as sustainable resources for production of bioplastics – A review. *J. Clean. Prod.* 162, 646–664.
3. Espro, C., Paone, E., Mauriello, F., Gotti, R., Uliassi, E., Bolognesi, M.L., Rodríguez-Padrón, D., and Luque, R. (2021). Sustainable production of pharmaceutical, nutraceutical and bioactive compounds from biomass and waste. *Chem. Soc. Rev.* 50, 11191–11207.

4. Jing, Y., Guo, Y., Xia, Q., Liu, X., and Wang, Y. (2019). Catalytic production of value-added chemicals and liquid fuels from lignocellulosic biomass. *Chem* 5, 2520–2546.
5. Zhu, J., and Yin, G. (2021). Catalytic transformation of the furfural platform into bifunctionalized monomers for polymer synthesis. *ACS Catal.* 11, 10058–10083.
6. Tiseo, I. (2021). Plastic production forecast worldwide 2025–2050. Statista. <https://www.statista.com/statistics/664906/plastics-production-volume-forecast-worldwide/>.
7. Jambeck, J.R., Geyer, R., Wilcox, C., Siegler, T.R., Perryman, M., Andrady, A., Narayan, R., and Law, K.L. (2015). Marine pollution. Plastic waste inputs from land into the ocean. *Science* 347, 768–771.
8. Woodruff, M.A., and Huttmacher, D.W. (2010). The return of a forgotten polymer—polycaprolactone in the 21st century. *Prog. Polym. Sci.* 35, 1217–1256.
9. Tang, X., and Chen, E.Y.-X. (2018). Toward infinitely recyclable plastics derived from renewable cyclic esters. *Chem* 5, 284–312.
10. Zhao, Z., Gao, G., Xi, Y., Wang, J., Sun, P., Liu, Q., Yan, W., Cui, Y., Jiang, Z., and Li, F. (2022). Selective and stable upgrading of biomass-derived furans into plastic monomers by coupling homogeneous and heterogeneous catalysis. *Chem* 8, 1034–1049.

Film formation mechanism uncovered in 2D/3D mixed-dimensional lead halide perovskites

Giuseppe Portale^{1,*}

2D layered metal halides can be added to 3D perovskites to improve the long-term stability of hybrid perovskite solar cells. The presence of the low-dimensional material alters the film formation mechanism. In this issue of *Chem*, Kanatzidis and collaborators investigate *in situ* the crystallization mechanism of mixed-dimensional 2D/3D lead-based perovskite films.

The energy crisis we have been facing in recent years and months calls urgently for the development and widespread use of alternative solutions to

fossil fuels. Among the various renewable energy solutions, conversion devices based on solar energy are regarded as the most viable solutions

to solve this crisis while strongly limiting the environmental pollution from carbon dioxide. Well-established, commercial photovoltaic technologies employ silicon to transform sunlight into electricity. However, the need for higher efficiency per unit area utilized stimulates the search for other materials that are easier to fabricate.

Currently, the field of photovoltaic technology is experiencing exciting times, and emerging technologies are

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being investigated with materials such as conjugated molecules and polymers, quantum dots, and perovskites.¹ In particular, metal halide perovskites are about to transform the next-generation photovoltaic technology—they exhibit efficiencies close to those of silicon-based solar cells at the lab scale and keep the production costs low because of the moderate temperature involved in their processing. Perovskites are 3D crystalline materials with an ABX_3 crystal structure in which A is a small monovalent ammonium cation, such as methylammonium (MA), formamidinium (FA), or cesium, occupying the cavity of the inorganic octahedra; B is a divalent metal cation, such as lead (Pb) or tin (Sn), sitting in the body center of the inorganic octahedra; and X is a halide anion (Cl^- , Br^- , or I^-) sitting at the corner of the BX_6 octahedra.

However, some major challenges need to be solved before metal halide perovskite solar cells can be commercialized. Among these challenges are the poor material stability under environmental stresses such as humidity and temperature and the difficulty of controlling the crystallization dynamics to eliminate structural disorder and unwanted phases when perovskite films are processed from solution.

One of the effective strategies for overcoming these two challenges is to replace the small monovalent ammonium cations in the perovskite structure with larger, bulkier hydrophobic cations, such as aliphatic or aromatic mono-, di-, or tri-ammonium cations. In particular, the bulky organic mono-ammonium cations (A') act as a spacer between the inorganic octahedra sheets, promoting the formation of a layered structure known as the Ruddlesden-Popper perovskite (RPP) structure. This concept was first introduced in 2014 by Karunadasa and co-workers, allowing the deposition of perovskite films from solution at ambient humidity

levels.² These layered RPPs have the generic formula of $(A')_2(A)_{n-1}BnX_{3n+1}$, where n is the number of inorganic octahedral layers separated by the bilayer of bulky or long A' cations, such as 2-phenylethylammonium ($C_6H_5C_2H_4NH_3^+$, PEA⁺) and *n*-butylammonium ($n-C_4H_9NH_3^+$, BA⁺). Initially, low- n (such as 3–5) members were produced and tested in the solar cell, providing a power conversion efficiency (PCE) of about 4.7%. After this seminal work, many research groups have worked hard to control the orientation, composition, and distribution of the RPP phase and improve the film morphology. In about 7 years since the 2014 work of Karunadasa and co-workers, the PCE of RPP solar cells has been boosted up to above 21% thanks to careful control of the structure and orientation of these 2D perovskite phases.³

Although single crystals can be obtained for the RPP with $n = 1-7$, it is generally very difficult to obtain phase-pure thin films because films made of these 2D materials show complex behavior and are composed of many phases with different n values, so the final composition depends on the employed fabrication method.⁴ In 2021, phase-pure films processed from solution were reported for $n = 1-5$ when strong coordination from a molten salt spacer, such as *n*-butylamine acetate, was used instead of the traditional halide spacer *n*-butylamine iodide (BAI) in the precursor formulation.⁵

The phase control for large n values ($n > 8$) becomes quite challenging, and the final films are composed of both 2D and 3D phases. In this case, we refer to the average n value ($\langle n \rangle$) of the precursor solution rather than the n value of the final film. These systems are often called mixed 2D/3D systems rather than RPP and are composed of a large part of an oriented 3D-like phase and a smaller fraction of an RPP phase. Mixed 2D/3D

phases have achieved >18% PCEs and long-term stability when exposed to humid conditions.⁶

In all of these works, of paramount importance in achieving high PCEs is control over the perovskite film structure, which can be achieved by modification of the chemistry of the system or the film manufacturing. In this respect, the availability of structural characterization techniques enabling quantitative and non-destructive measurements is crucial. Among the possible techniques, grazing-incidence wide-angle X-ray scattering (GIWAXS) is the perfect candidate because it allows quantitative investigation of the film structure (revealed by the diffraction peak position) and investigation of the crystallite orientation through measurement of partial pole figures.⁷ Moreover, when performed at high-brilliance synchrotrons, GIWAXS analysis can be performed *in situ* during spin coating or blade coating of perovskites, offering unique results to elucidate the mechanism of crystallization during film processing (Figure 1, top). In recent years, *in situ* GIWAXS has been successfully applied to RPP⁸ and mixed 2D/3D systems.⁹

Building on the recent development of *in situ* GIWAXS for perovskite crystallization, as recently published in *Chem*, Kanatzidis and co-workers studied in detail the film formation process during spin coating of mixed 2D/3D dimensional systems prepared from precursor solutions of $(BA)_2(MA)_{n-1}Pb_nI_{3n+1}$ with different stoichiometry ($n = 3, 4, 5, 7, 12, 50, \text{ and } \infty$ [MAPbI₃]).¹⁰ Quantitative analysis of the GIWAXS patterns acquired with millisecond time resolution revealed two possible fundamental mechanisms: the “orientation mechanism” characteristic of the low $\langle n \rangle$ stoichiometry ($\langle n \rangle = 3$) and the “solvate mechanism” characteristic of the pure 3D MAPbI₃ perovskite (Figure 1, bottom). The first mechanism

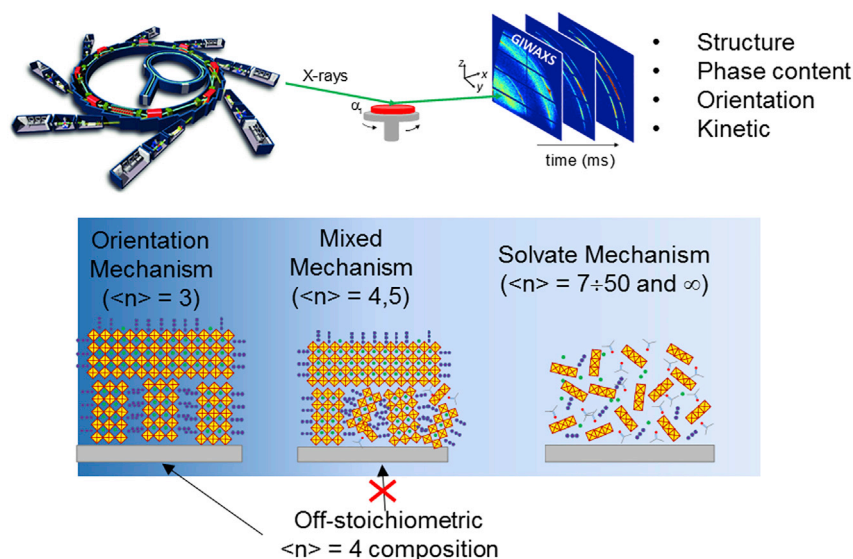


Figure 1. Schematic of the film formation mechanism in 2D/3D Pb-based perovskites using *in situ* X-ray scattering

(Top) Synchrotron light enables *in situ* GIWAXS measurements during spin coating.

(Bottom) Schematic of the mechanism of crystallization occurring during film formation in 2D/3D mixed-dimensional lead-based halide perovskite films. $\langle n \rangle$ represents the stoichiometry of the system according to the chemical formula $(\text{BA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$, where BA is butylammonium and MA is methylammonium.

leads to the formation of a 3D-like structure at the air-liquid interface that templates the perpendicular growth of the $n = 3$ pure phase. The solvate mechanism leads to the formation of poorly oriented $(\text{MA})_2\text{Pb}_3\text{I}_8 \times 2\text{DMF}$ solvated crystals that can be transformed into a perovskite structure only upon annealing. Films casted from a nominal precursor composition of $\langle n \rangle = 4-5$ crystallize after the two mechanisms, such that the solvate mechanism interferes with the initial orientation mechanism. The solvent mechanism is solely observed for $\langle n \rangle \geq 7$. Minor fractions of crystallites with $n = 2$ and $n > 3$ are also found in these films. The knowledge of these mechanism reveals important differences from alternative perovskites, such as thin-based 2D/3D ones, where the solvate mechanism is not observed and the orientation mechanism leads to an $n = 2$ phase with parallel orientation.⁹ Suppression of the solvate mechanism in Pb-based perovskite is essential because it allows a high

perpendicular crystallite orientation and avoids pinhole-rich needle-like film morphology.

Using the *in situ* information gained on the crystallization mechanism, the work of Kanatzidis and co-workers shows how the use of a simple off-stoichiometric formulation with an excess of MAI (methylammonium iodide) suppresses the undesirable solvate mechanism. The off-stoichiometry method adds up to the spectrum of already known methods available for researchers to improve film quality and achieve the preferred crystallite orientation, such as hot casting and solvent engineering.

Overall, the study by Kanatzidis and co-workers highlights the importance of collecting *in situ* structural data during the formation of perovskite film. The knowledge of the crystallization mechanism is not for mere scientific curiosity but is rather crucial for tuning the perovskite precursor formulation in order to control phase content,

phase distribution, and crystallite orientation and thus achieve improved performances in 2D/3D mixed-dimensional perovskite systems over a wide range of stoichiometries. My perspective is that, with the help of time-resolved *in situ* X-ray analysis applied to lab- and industrial-scale processing, researchers will continue to boost the performance and stability of perovskite solar cells, paving their way toward commercialization of this future photovoltaic technology.

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DECLARATION OF INTERESTS

The author declares no competing interests.

- Almora, O., Baran, D., Bazan, G.C., Berger, C., Cabrera, C.I., Catchpole, K.R., Erten-Ela, S., Guo, F., Hauch, J., and Ho-Baillie, A.W. (2021). Device performance of emerging photovoltaic materials (version 2). *Adv. Energy Mater.* *11*, 2102526. <https://doi.org/10.1002/aenm.202102526>.
- Smith, I.C., Hoke, E.T., Solis-Ibarra, D., McGehee, M.D., and Karunadasa, H.I. (2014). A layered hybrid perovskite solar-cell absorber with enhanced moisture stability. *Angew. Chem. Int. Ed.* *53*, 11232–11235. <https://doi.org/10.1002/anie.201406466>.
- Shao, M., Bie, T., Yang, L., Gao, Y., Jin, X., He, F., Zheng, N., Yu, Y., and Zhang, X. (2022). Over 21% efficiency stable 2D perovskite solar cells. *Adv. Mater.* *34*, e2107211. <https://doi.org/10.1002/adma.202107211>.
- Shao, S., Duim, H., Wang, Q., Xu, B., Dong, J., Adjokatse, S., Blake, G.R., Protesescu, L., Portale, G., Hou, J., et al. (2020). Tuning the energetic landscape of Ruddlesden-Popper perovskite films for efficient solar cells. *ACS Energy Lett.* *5*, 39–46. <https://doi.org/10.1021/acsenenergylett.9b02397>.
- Liang, C., Gu, H., Xia, Y., Wang, Z., Liu, X., Xia, J., Zuo, S., Hu, Y., Gao, X., and Hui, W. (2021). Two-dimensional Ruddlesden-Popper layered perovskite solar cells based on phase-pure thin films. *Nat. Energy* *6*, 38–45. <https://doi.org/10.1038/s41560-020-00721-5>.

6. Yang, R., Li, R., Cao, Y., Wei, Y., Miao, Y., Tan, W.L., Jiao, X., Chen, H., Zhang, L., Chen, Q., et al. (2018). Oriented quasi-2D perovskites for high performance optoelectronic devices. *Adv. Mater.* 30, e1804771. <https://doi.org/10.1002/adma.201804771>.
7. Schlipf, J., and Müller-Buschbaum, P. (2017). Structure of organometal halide perovskite films as determined with grazing-incidence x-ray scattering methods. *Adv. Energy Mater.* 7, 1700131. <https://doi.org/10.1002/aenm.201700131>.
8. Quintero-Bermudez, R., Gold-Parker, A., Proppe, A.H., Munir, R., Yang, Z., Kelley, S.O., Amassian, A., Toney, M.F., and Sargent, E.H. (2018). Compositional and orientational control in metal halide perovskites of reduced dimensionality. *Nat. Mater.* 17, 900–907. <https://doi.org/10.1038/s41563-018-0154-x>.
9. Dong, J., Shao, S., Kahmann, S., Rommens, A.J., Hermida-Merino, D., ten Brink, G.H., Loi, M.A., and Portale, G. (2020). Mechanism of crystal formation in Ruddlesden-Popper Sn-based perovskites. *Adv. Funct. Mater.* 30, 2001294. <https://doi.org/10.1002/adfm.202001294>.
10. Hoffman, J.M., Hadar, I., Li, X., Ke, W., Vasileiadou, E.S., Strzalka, J., Chen, L.X., and Kanatzidis, M.G. (2022). Film formation mechanisms in mixed-dimensional 2D/3D halide perovskite films revealed by in situ grazing-incidence wide-angle X-ray scattering. *Chem* 8, 1067–1082. <https://doi.org/10.1016/j.chempr.2021.12.022>.

Self-assembly of a large, closed capsule reminiscent of protein-cage formation

Dawei Zhang^{1,*} and Hai-Bo Yang^{1,*}

In this issue of *Chem*, Nitschke and co-workers report on a new type of tetrahedral cage where, unlike in conventional metal-organic capsules (in which individual ligands define the faces or edges of a polyhedron), each face of the capsule is spanned by three ligand panels, reminiscent of ferritin capsule formation. They achieve this concept through the self-assembly of a simple twisted tetramine subcomponent. Moreover, the resulting large, enclosed cavity is able to accommodate multiple equivalents of large dianions.

Self-assembly is the key construction technique for making the higher-order structures of life. Protein cages are normally formed by the self-assembly of multiple protein subunits. Ferritin is a typical example: it exhibits a roughly spherical cage structure whose vertices are spanned by multiple protein subunits.¹ In nature, the cavity of ferritin is utilized for the sequestration and release of iron in a controlled fashion. An attractive goal of synthetic chemists is the construction of self-assembled architectures that resemble the structures of protein cages. However, most of the cases reported so far have focused on the size and shape of the capsule rather than how the protein cage forms. Coordination-driven self-assembly is an efficient tool for the construction of diverse organometallic supramo-

lecular architectures.² One subset of these structures, metal-organic polyhedral complexes, has proven useful in a range of applications, from separation³ to catalysis.⁴

Recently, more attention has been paid to the synthesis of large and complex capsules, which can bind and release large payloads and mimic the structures and functions of protein cages. Usually, the challenge in constructing large capsules originates from both the difficulty of the synthesis of large ligands and the increased entropic penalty incurred in the assembly of large capsules with greater nuclearity. Foundational work by Fujita et al.⁵ and others^{6,7} provides successful examples of large metal-organic capsules assembled from high-symmetry

building blocks by judicious design. These known polyhedra often have regular Platonic (faces consisting of one regular polygon) or Archimedean (faces consisting of two or more regular polygons) geometries, where individual subunits define the faces or edges of the polyhedron. Such structures tend to be porous with very open cavities, thus leading to poor guest binding properties.

In this issue of *Chem*, Nitschke and co-workers report on the self-assembly of a large tetrahedral metal-organic cage via subcomponent self-assembly.⁸ Instead of single ligands spanning its vertices, each face of the tetrahedron is paneled by three ligands, mimicking the arrangement of the subunits of a ferritin cage. The cavity of this new capsule is large and enclosed, and the structure was observed to bind multiple equivalents of $\text{Mo}_6\text{O}_{19}^{2-}$ in solution.

Subcomponent self-assembly is a strategy for preparing metal-organic architectures, the building blocks of which come together through the formation of coordinative (N → metal) and covalent (N=C) bonds during a single self-assembly process.⁹ The self-assembly

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