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Perspective

The making of a reconfigurable semiconductor with a soft ionic lattice

Mengyu Gao,[1,2] Ye Zhang,[2,3] Zhenni Lin,[1,2] Jianbo Jin,[3] Maria C. Folgueras,[1] and Peidong Yang[1,2,3,4,*]

SUMMARY

Synthetic understanding is crucial for designing halide perovskites with controlled properties and for paving ways to create a new family of structures. With expanding synthetic approaches, it is especially necessary to elucidate the formation of halide perovskites and how that influences their associated properties to inform a unifying design principle. In this perspective, we summarize key milestones in the synthesis community of inorganic halide perovskite nanostructures and highlight how the reaction kinetics and thermodynamics of halide perovskites distinguish them from traditional inorganic semiconductors. We then present a retrospective view that conceptually unites physical chemistry theories with advanced synthesis and address lingering questions in the field along with possible solutions. This perspective aims to articulate the relation between structural properties, synthetic tunability, and the environmental stability of halide perovskites and to provide an outlook for new generations of halide perovskite nanostructures for efficient and stable devices.

INTRODUCTION

Halide perovskites have achieved remarkable optoelectronic performance over the past decade, with notable applications in solar cells, light-emitting diodes (LEDs), and lasers,[1–4] because of their solution processability, ease of fabrication, and extraordinary physical properties. The facile synthesis has produced nanoscale and macroscale perovskites across dimensionality, composition, and crystal structures, further diversifying their applications and prompting fundamental studies to probe this new class of semiconductor. As synthesis closely governs the final products and the associated properties, it goes without saying that a comprehensive understanding of the synthetic pathways and design principles is crucial.

All-inorganic halide perovskites have gained special attention due to their enhanced stability over hybrid perovskites. Since the first nanocrystal synthesis reports of all-inorganic halide perovskites,[5–7] synthesis-related studies have covered almost every domain of nanostructure engineering, including size and morphology control, ion exchange, chemical doping, heterostructures, ligand engineering, and structure evolution. Although review papers of various lengths and topics are abundant in the literature,[8–10] a general framework that coherently incorporates the fundamental structural properties, synthetic methods, and characterization tools is still missing. A starting point for addressing this conceptual task is to review the difference between halide perovskites and traditional covalent semiconductors (Table 1; Figures 1A and 1B), especially the fact that ionic crystals have lower cohesive energies compared with traditional covalent semiconductors (2–3 eV per atom for typical ionic crystals and halide perovskites, but >4 eV per atom for covalent semiconductors such as

Progress and potential

Rapid synthetic advancements in halide perovskites have spurred a growing family of new compositions, crystal structures, and properties. The facile synthesis can be attributed to the soft and flexible lattice of halide perovskites, a property that yields low-temperature synthesis, mobile ions, and easily configurable structures. However, in order to achieve products with controlled properties, there must exist a design principle that unites physical chemistry theories with advanced synthesis, a principle that is presently absent from the existing literature. This perspective examines the existing synthetic advances, limitations, and understanding of the lattice to call for such a design principle for halide perovskite nanostructures. The future directions outlined in this perspective present guiding principles to design the next generations of halide perovskite nanostructures with new functional properties, stability, and complexity for fundamental studies and device applications. Furthermore, the framework and principles presented in this perspective may also be applied more generally to the synthesis of other semiconducting materials with soft lattices.

Table 1. Comparative study of the structural properties of conventional semiconductors and halide perovskites

	Conventional semiconductors	Halide perovskites
Bulk properties		
Bonding type	covalent, ionic	ionic
Cohesive energy	>4 eV/atom	3 eV/atom
Melting point	above 1,000°C	below 600°C
Solubility	insoluble in solvents	soluble in polar solvents
Nanostructure properties		
Synthesis temperature (solution phase)	above 300°C	below 150°C
Synthesis temperature (vapor phase)	mostly above 1,000°C for both evaporation and deposition	400°C–600°C for evaporation; 100°C–400°C for deposition
Growth kinetics	slow	fast even at low temperature
Incorporation with organic components	only on the surface (nanocrystals)	in the lattice (hybrid or 2D perovskite) or on the surface (nanocrystals)
Heterostructure	can interface with another covalent semiconductor by epitaxial growth when lattice mismatch is small	can accommodate large lattice mismatch; facile creation of heterostructures by post-synthesis

Si).[11,12] However, this comparison is only superficially useful if not viewed through an integrated perspective where the ideas and theories of structure, synthesis, and characterization are on equal footing. The uniqueness of halide perovskites has its origin in its chemical bonding and ionic framework, which impart synthetic flexibility but also long-term environmental instabilities. Addressing the remaining challenges and providing insights for future rational synthesis and engineering require a retrospective review of the synthetic development, a conceptual articulation between theories and experimental observations, and perspectives open for future modifications in light of new synthetic achievements.

This perspective, in alignment with other Pieces Perspectives in this issue, is divided into four sections. In the "past" section, we summarize key milestones in the synthesis community of inorganic halide perovskites, with an emphasis on the synthesis of nanostructures. In the "present" section, we present a retrospective study that unites physical chemistry theories with advanced synthesis, which is typically missing in early synthesis-related literature. In the "problems" section, we raise lingering questions and challenges in the synthetic community. Finally, in the "possibilities" section, we attempt to bridge the gaps between the structural properties, synthetic tunability, and environmental stability of halide perovskites, and provide an outlook for new generations of halide perovskite nanostructures.

PAST: TYPICAL SYNTHETIC METHODS

In the past 10 years, the community has witnessed great advances in the synthesis of all-inorganic halide perovskites. In particular, enormous scientific efforts have been devoted to the synthesis of nanocrystals, thin films, bulk single crystals, and heterostructures. In this perspective, we focus on the synthetic methods for single crystalline and heterostructure nanocrystals/microcrystals.

Colloidal synthesis, with the assistance of capping ligands, can produce an ensemble of uniform nanocrystals. Based on a similar hot-injection method borrowed from II–VI quantum dots synthesis, the synthesis of $CsPbX_3$ nanocrystals with a uniform size distribution was first reported in 2015,[5–7] and, since then, various synthetic routes to control

[1]Department of Materials Science and Engineering, University of California, Berkeley, Berkeley, CA 94720, USA

[2]Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

[3]Department of Chemistry, University of California, Berkeley, Berkeley, CA 94720, USA

[4]Kavli Energy NanoScience Institute, Berkeley, CA 94720, USA

*Correspondence: p_yang@berkeley.edu

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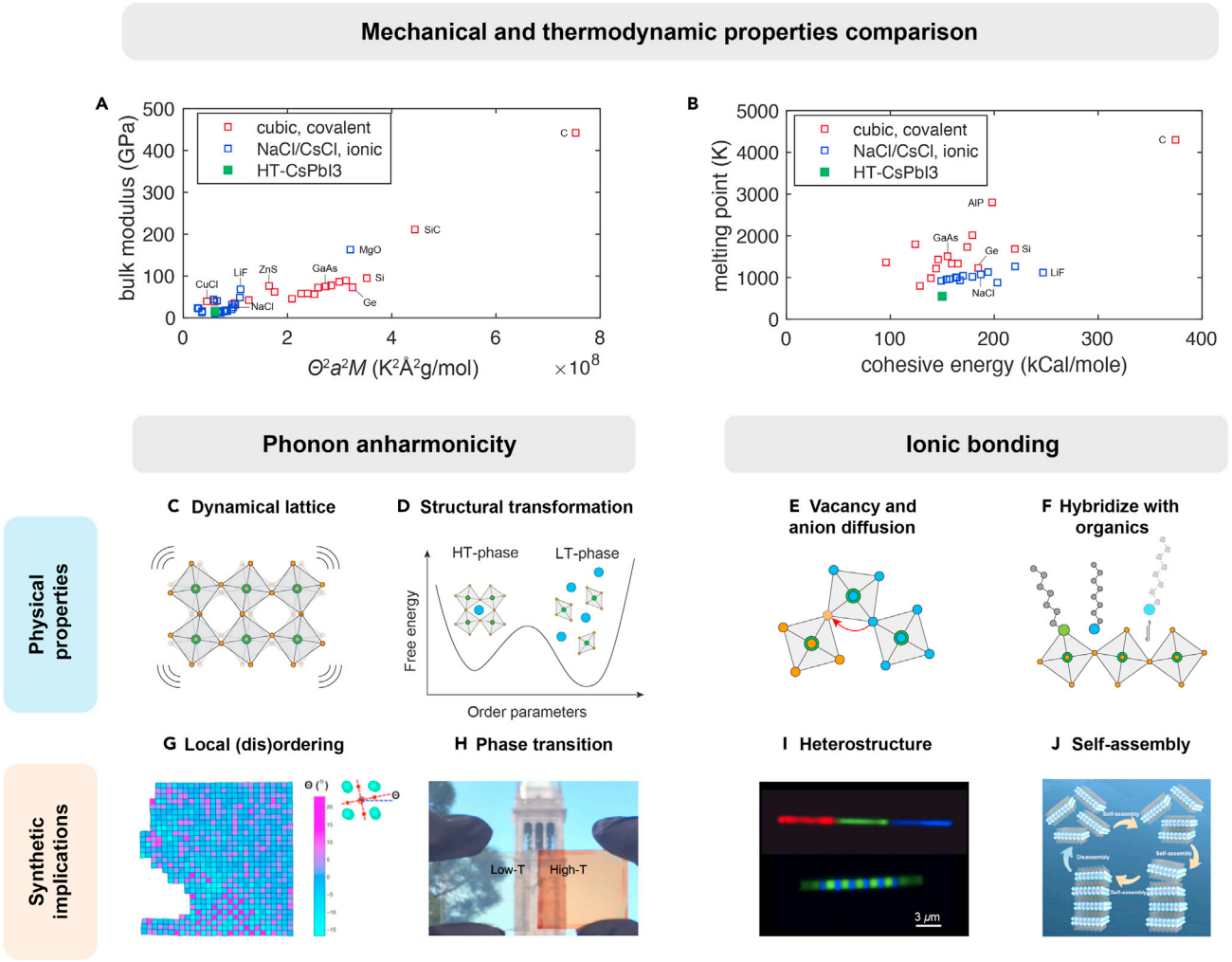

Figure 1. Connecting fundamental structural properties with synthetic implications of halide perovskites

(A) Relation between bulk modulus and renormalized Debye temperature of different semiconductors and insulators (traditional cubic semiconductors with diamond or zinc blende crystal structures, and ionic crystals with either NaCl or CsCl structures are selected to compare with HT $CsPbI_3$), where Θ is the Debye temperature, which is related to the lattice dynamics of the material, a is the lattice constant, and M is the averaged atomic weight.[12–14]

(B) Relation between melting temperature and cohesive energy of different semiconductors and insulators.[15]

(C–F) Schematic illustrations of unique structural properties of halide perovskites.

Schematic illustrations of synthetic implications of the structural properties of halide perovskites.

(G) Local octahedral distortion in $CsPbBr_3$ nanoplates.[16] Copyright 2016 American Chemical Society.

(H) Phase transition-induced thermochromic solar cells.[17] Copyright 2018, the Author(s) 2018, under exclusive license to Macmillan Publishers Limited, part of Springer Nature.

(I) Anion exchange reaction-induced $CsPbX_3$ heterostructures.[18] Copyright 2017 National Academy of Sciences.

(J) Self-assembly of perovskite nanocrystal building blocks.[19] Copyright 2019 American Chemical Society.

morphology, size, facet exposure, and phase or composition have been developed (Figures 2A–2D).[8,9,20] Although the synthetic conditions of halide perovskites resemble those of covalent semiconductor nanocrystals, the studies following the first colloidal synthesis of perovskite nanocrystals reveal the distinct thermodynamic properties of halide perovskites, such as relatively low reaction temperature, easily achieved morphology tunability, and dynamical ligand shells.

In contrast to colloidal synthesis, ligand-free solution-phase synthesis of halide perovskite nanostructures makes use of a substrate-assisted dissolution-recrystallization

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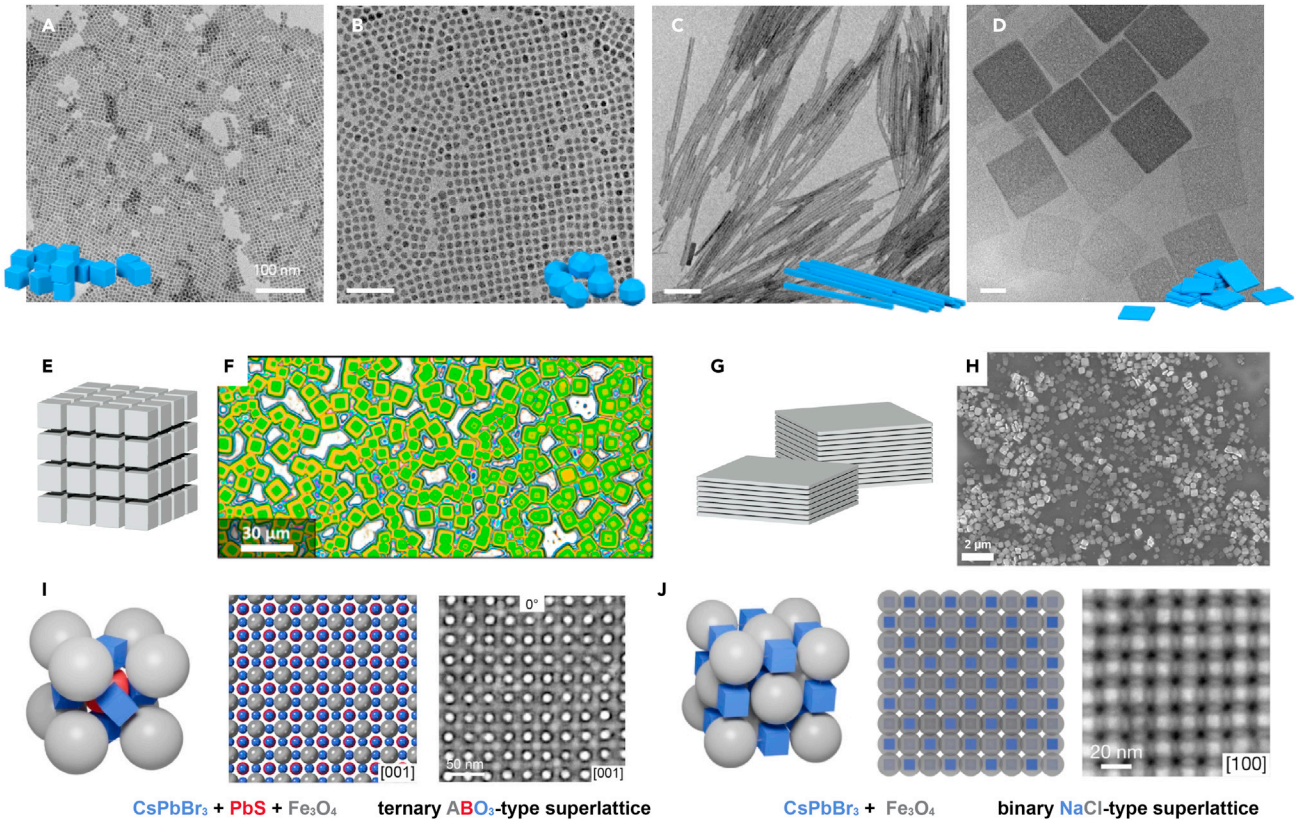

Figure 2. Nanocrystal building blocks and their self-assembly

(A–D) Colloidally synthesized cesium-lead-bromide nanocubes, rhombic dodecahedrons, nanowires, and nanoplates, respectively, as nanoscale building blocks.[19–21] Copyright 2019 American Chemical Society.

(E and F) Self-assembly of $CsPbBr_3$ nanocubes into a simple-cubic superlattice.[22] Copyright 2021 American Chemical Society.

(G and H) Self-assembly of nanoplates into RP phase structures.[19] Copyright 2019 American Chemical Society.

(I and J) Self-assembly of $CsPbBr_3$ nanocrystals with other nanocrystals to form binary or ternary superlattices with different lattice types.[23] Copyright 2021 Springer Nature.

process.[3] The lead halide thin film, which acts as both the precursor source and nucleation sites, is immersed into a diluted cesium halide solution. The dissolved lead halide and cesium halide precursors then react and slowly recrystallize to form halide perovskite. This simple solution-phase synthesis technique can produce a variety of inorganic halide perovskite compositions in nanostructured forms, including $CsPbBr_3$, $CsPbI_3$, $CsSnI_3$, and their alloys.[3,24,25]

Vapor-phase synthesis, which includes epitaxy, deposition, and crystal growth, provides another facile route to obtaining nanoscale/microscale single crystals and thin films of halide perovskites.[26–31] In contrast to that of traditional semiconductors,[32,33] vapor-phase synthesis of halide perovskites typically requires lower temperatures and can be achieved via a simple one-step chemical vapor transport (CVT) or a physical vapor deposition technique without the need of additional reactive transport agents or forming gaseous intermediates thanks to the relatively volatile halogen elements in the precursors and end products. The vapor-phase synthesis can be performed in a tube furnace[27] or thermal evaporation chamber[34] using either dual sources or only one source by mixing the precursors in appropriate stoichiometric ratios, under a flow of inert gas (Ar or N_2)[29,30,35] or under vacuum.[31] Reports of vapor-phase synthesis of halide perovskites over the past 5 years have revealed a flexible control

of dimensions, morphologies, compositions, and structural phases of nanoscale/microscale pure single crystals as well as the growth of large-area thin films.[26,27,29,30,35] The dependence of such growth controllability on the choice of substrate (e.g., epitaxy/non-epitaxy; lattice mismatch-induced strain) is an important question to be investigated, as the chosen substrates (with different crystal structures or lattice parameters) can greatly impact the morphological control, phase stability, and band-gap modulation of the as-grown perovskites.

Post-synthetic methods, such as anion exchange reactions, provide flexible ways to further modify the compositional, electronic, and structural properties of halide perovskite nanostructures. In anion exchange reactions, a parent ABX_3 is exposed to an abundant source of precursor that contains another halide species (either in the solution phase or vapor phase), creating an anion concentration gradient. The concentration gradient then drives the diffusion of the guest ions into the parent lattice to achieve partial or complete replacement of the parent anion. Notable examples of anion exchange reactions include colloidal nanocrystals with tunable compositions and dimensionalities,[7,36–38] and heterostructures with well-defined physical properties separated by sharp interfaces.[18,30,39] In the cases where direct synthesis is difficult, post-synthetic methods also provide a route to make thermodynamically unstable nanostructures.[38]

PRESENT: STRUCTURAL PROPERTIES AND ADVANCED SYNTHETIC CONTROL

Scientific development is not always a linear process. A simplistic perspective detailing only the synthetic advancements and structural understanding of halide perovskites conceals both the complexities of scientific research as an iterative enterprise and the perplexities of the structural characteristics of halide perovskites in particular. To understand the present state of the synthetic development in the field, we need to extract from the literature a new conceptual framework that is not anticipated for traditional covalent semiconductors, from which we can derive a rational route for better synthetic control and engineering.

Figure 1 presents a three-level account aiming to address the synthesis-related topics. In the first level, we highlight the key conceptual building blocks that "synthesize" the current research paradigm within the halide perovskite community, which is to understand the softness of halide perovskites. This fundamental conception of lattice softness (gray-shaded boxes in Figure 1) is followed by a discussion of the ensuing physical properties, such as a dynamic lattice, high anion diffusivity, and phase transition behaviors (Figures 1C–1F). Finally, in the last level, these physical properties inform advanced synthetic control or engineering (Figures 1G–1J).

Soft lattice of halide perovskites

Throughout this perspective, we demonstrate that the synthetic flexibility of halide perovskites and the stability of their nanostructures are directly related to their unique structural properties, which have primary origins in (1) the molecular bonding characteristics, (2) stereochemically active ns^2 electron lone pairs of Pb or Sn atoms, and (3) their tolerance factor deviating from unity as a reason to account for structural instabilities—but this geometrical factor might be partially absorbed into the energetic consideration of the stabilized ns^2 electrons.[40] To understand the synthetic mechanism and provide insight into a better synthetic strategy, an investigation of the fundamental structural properties is essential.

Ionic bonding as the major cohesive interaction in halide perovskites makes them highly soluble in most solvents and thus solution processable. Since the cohesive energy of a crystal inversely scales with its ionicity,[41] lower melting points are expected for solid-state synthesis or vapor-phase synthesis of halide perovskites (Figure 1B). The weak chemical bonding combined with the intrinsically stereochemically active ns^2 lone pair contributes to the dynamic disorder and overdamped phonon dispersion in the high-symmetry halide perovskite lattice, and to the phase transitions to low-symmetry phases at different thermodynamic conditions (Figures 1C and 1D).[42,43] Not only is the material itself recognized as dynamically disordered, but the interface that mediates phase transitions is also predicted to be liquid-like.[44] The lower cohesive energy of the lattice and weaker chemical bonds also point to a higher vacancy concentration and faster anion diffusion (Figure 1E).

The nondirectional nature of the ionic bonding allows organic cations to be incorporated into halide perovskite lattices, which offers a large degree of structural tunability (Figure 1F). The organic components can either be incorporated into the lattice, as in the case of hybrid organic-inorganic perovskites and 2D Ruddlesden-Popper-phase perovskites, or they can occupy terminating sites on the surface of nanocrystals. The presence of organic components in halide perovskite crystals further lowers the mechanical strength and melting point of the material, and improves the solution processabilities. In particular, the organic ligand shell plays a vital role in defining the structural integrity of halide perovskite nanocrystals. Different from typical II–VI semiconductor nanocrystals, where the higher cohesive energy of the inorganic component outweighs the energetic contribution from the organic ligands, the hybrid nature of halide perovskites requires us to view the inorganic nanocrystal and the ligands as a whole. Not only should the ligand-surface interaction be considered, but the intermolecular interaction within the ligand shell should also be carefully studied.

The chemical bonding characteristics and stereochemically active ns^2 electron configuration cause the ionic perovskite lattice to have lower mechanical strength, lower melting points, facile solution processability, and rich phase diversity. Their interactive nature to hybridize with organic components makes the perovskite lattice less rigid or less statically defined compared with traditional semiconductors, and therefore easier to reconfigure. In this context, we contrast the structure of halide perovskites with that of traditional semiconductors by highlighting the soft, reconfigurable halide perovskite lattice. In the following text, we now demonstrate from a physical chemistry perspective that the conceptual definition of "softness" can manifest in different ways in the synthesis and be examined and measured quantitatively.

Structural dynamics and their implications in synthesis

Growth kinetics and self-assembly of halide perovskite nanocrystals

The soft lattice of perovskites enables facile synthesis of nanostructures of various dimensionalities, sizes, and aspect ratios under conditions milder than those needed for traditional semiconductors. In solution-phase synthesis, the high ionic solubility of precursors in polar solvents results in synthesis temperatures that are typically lower than 150°C, or even as low as room temperature. In addition, the reaction kinetics during the synthesis of halide perovskites are considerably faster compared with those of traditional semiconductors under the same temperature. For example, the growth rate of halide perovskite nanowires was quantified to be 4 nm/s at 125°C[21] and 1 μm/min in the lateral direction of CVT-grown plates/films at ~550°C.[31] Although at higher temperatures (1,050°C), GaN nanowires can grow as fast as 300 nm/s, the growth of a unit cell of the GaAs nanowire at mild

temperatures (400°C) proceeds at only several angstroms per second.[45] The drastic difference in their growth kinetics provides a simple contrast between the synthetic conditions of halide perovskites and those of typical semiconductors, which, as we have stated, originates from the different chemical bonding types and cohesive energies of the crystals.

In such a fast kinetically controlled growth condition, anisotropic growth may be favored; therefore, the syntheses of 1D and 2D perovskite nanostructures were reported almost simultaneously with those of the 0D symmetric geometry.[6,7] These 1D and 2D nanostructures have been used as great platforms to quantitatively study mass transport (e.g., anion diffusion, thermal transport), structural evolution (e.g., phase transition propagation), and electronic transport (e.g., carrier dynamics), some of which is detailed in this section.

The hybrid nature of halide perovskites implies a strong coupling between the inorganic framework and the organic components through interfacial ionic bonding as well as global energetics. For inorganic perovskite nanocrystals, the surface ligands constitute a dynamic screening barrier from the solvent environment. Instead of a strong covalent bonding toward the inorganic surface, typical ligands for halide perovskites exhibit dynamic binding kinetics. Quantitative diffusion ordered NMR spectroscopy revealed a significantly higher diffusion coefficient for the perovskite surface ligands compared with that expected for tightly bound ligands.[46] Nuclear Overhauser effect NMR spectroscopy (NOESY) is another quantitative technique to resolve the dynamic interaction between ligands and nanocrystal surfaces, where the sign of the cross-peaks in the 2D spectrum is related to the tumbling frequency of the ligands (Figure 4B).[47] This dynamic ligand shell is effective only in a time-averaged sense to annihilate the surface defects. Trapping and detrapping of photogenerated carriers therefore accompany the chemical process of ligand adsorption and desorption.[21,48] To address the balance between the dynamic ligand binding and the fragile lattice of halide perovskites, and consequently to improve the solution stability and luminescence efficiency, a subtle control by selecting suitable acid-base-matched ligands has been rationally designed.[47,49,50]

A higher hierarchical level of synthesis is the assembly of nanocrystal building blocks. The uniform size and morphology control of perovskite nanocrystals have made possible the self-assembly of these nanoscale building blocks with various dimensionalities (Figures 2A–2D) into superlattices.[19,22,51,52] The cuboidal shape of typical 0D perovskite quantum dots has greatly improved the orientational order of the simple-cubic superlattice made from them (Figures 2E and 2F).[22,52] The great size homogeneity enables a high degree of translational and orientational order in perovskite nanocrystal superlattices, and such structural order gives rise to a coherent collective emission known as superfluorescence.[23,52] Atomically precise control over the perovskite nanocrystal thickness has also been demonstrated, where 2D halide perovskite nanosheets can be assembled into a well-ordered Ruddlesden-Popper phase (Figures 2G and 2H).[19]

Before the development of halide perovskite nanocrystals, spherical nanocrystals have been used as building blocks of nanocrystal superlattices. The emergence of cuboidal perovskite quantum dots enriches the library of nanocrystal superlattices by adding a new degree of freedom.[23] In addition to the single-component superlattices, combining halide perovskite nanocrystals with other types of nanocrystals can achieve binary or ternary superlattices with different lattice types. In a recent study (Figures 2I and 2J),[23] cubic $CsPbBr_3$ nanocrystals were combined with

spherical Fe_3O_4 or $NaGdF_4$ nanocrystals to form binary perovskite-type ABO_3 superlattices. The large Fe_3O_4 or $NaGdF_4$ nanocrystals occupy the A sites, and the smaller $CsPbBr_3$ nanocrystals occupy B and O sites. With the addition of PbS nanocrystals, ternary superlattices can also form. In this case, the B sites are occupied by PbS nanocrystals. It has been shown that the cuboidal perovskite nanocrystal shape with sharp edges is essential to the formation of ABO_3-type superlattices, which have not been realized previously in all-spherical systems. Flexible control over the nanocrystal compositions, shapes, and sizes has made possible a variety of other lattice types, such as NaCl-type and AlN_2-type lattices.

Anion diffusion and heterostructures

The rich and mobile vacancies in halide perovskites are one of the unique features of the flexible and reconfigurable perovskite lattice (Figure 1E). Among the different types of vacancies in halide perovskites, halide anion vacancies are the dominating vacancy species due to their lower formation energies (0.35–0.42 eV) compared with those of the other point defects.[53] Molecular dynamics (MD) simulations computed the anion vacancy concentrations to be 10^{-7}–10^{-9} per unit cell.[54] As a result of this unique defect physics, anion vacancies play an important role in the perovskite lattice dynamical behavior, including anion diffusion and phase transitions.

The intrinsically high anionic mobility and relatively rigid cationic sublattice enable fast anion exchange kinetics in halide perovskites, with the end products still maintaining the initial perovskite structure. While early anion exchange studies mainly focused on measurements of nanocrystal ensembles,[36,37,55] the recent emergence of synthetic platforms, such as well-defined anionic heterostructures,[18] coupled with *in situ* microscopic optical imaging methods, have been utilized to understand the anion exchange kinetics on the single-particle level and thus realize better engineering control of complex structures.[18,30,54,56] Investigations into the anion exchange kinetics from $CsPbBr_3$ to $CsPbI_3$ on individual nanoplates have decoupled the entire transformation into an initial surface reaction and a subsequent lattice anion diffusion, and identified that the anion diffusion inside the solid-state lattice is the rate-determining step (Figures 3A and 3B).[30] In addition, by monitoring a thermally induced anion diffusion in $CsPbCl_3$-$CsPbBr_3$ nanowire heterojunctions, the anion interdiffusivities were determined to be 10^{-13} to 10^{-12} cm^2/s at 75°C–125°C, and the activation energy for halide diffusion was determined to be 0.28 eV.[54] MD simulations suggest that the halide diffusion is mediated by vacancies, as the computed halide vacancy formation free energies are small and therefore give rise to the high equilibrium vacancy concentrations that lead to the high interdiffusivities. The intrinsic ion diffusion is facilitated by the soft lattice of halide perovskites because of the low barriers to vacancy hopping. In addition to the intrinsic anion diffusion driven by concentration gradient and temperature, an electric field has also been utilized to mobilize anions.[57] In this study, the electric field-driven ion migration exhibits ionic rectification, which is a consequence of the competition between electrical screening and the vacancy creation and destruction at the electrodes' interfaces. This new type of heterostructure engineering mediated by an electric field not only provides a new approach to control anionic heterostructures of halide perovskites, but also sheds light on the asymmetric ionic transport in solid-state systems in general.

After the formation of anionic heterostructures, long-term interfacial stability requires a dedicated, extrinsic control that suppresses the characteristic fast anion diffusion. Dou et al. reported a new epitaxial heterostructure by molecular-level engineering of halide perovskite quantum wells (Figures 3C and 3D).[39] The rigid conjugated organic ligands

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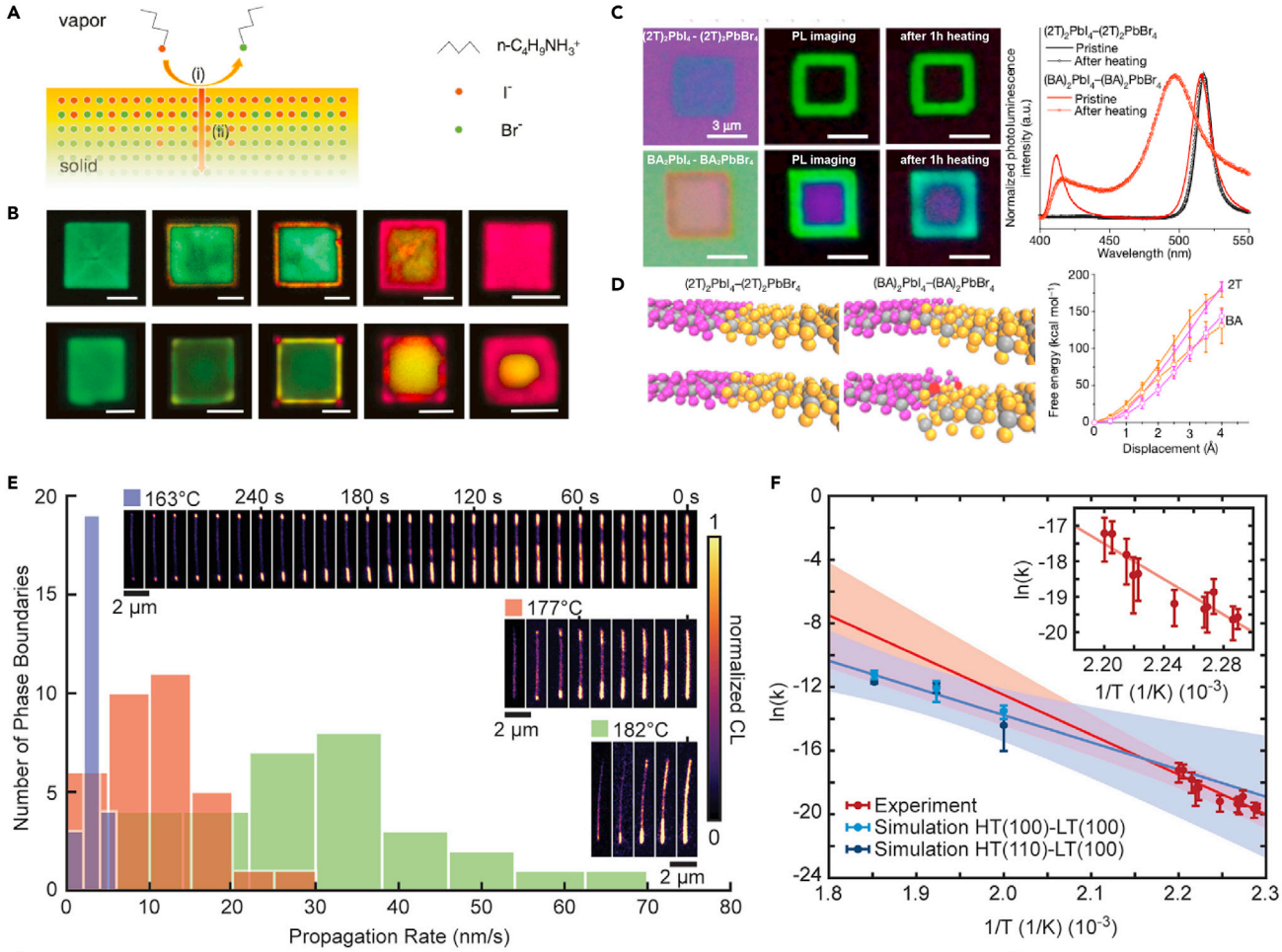

Figure 3. Anion exchange chemistry, phase transition kinetics, and heterostructures

(A) Schematic of the two-step anion exchange process: (i) surface reaction; (ii) solid-state ion diffusion.

(B) Photoluminescence (PL) imaging of the anion exchange process on individual nanoplates with dependence on time (from left to right) and plate thickness (from top to bottom). Scale bars, 5 μm.[21] Copyright 2019 National Academy of Sciences.

(C) Optical and PL images of two kinds of lateral heterostructures: $(2T)_2PbI_4$-$(2T)_2PbBr_4$ and $(BA)_2PbI_4$-$(BA)_2PbBr_4$, with the corresponding PL spectra (before and after heating) shown on the right.

(D) Snapshots from the molecular dynamics (MD) simulations at 298 K (top panel) and 800 K (bottom panel) for the two heterostructures, together with the plots of free energy for removing a halide atom to generate a halide vacancy (orange, bromide; purple, iodide).[39] Copyright 2020, the Author(s), under exclusive license to Springer Nature Limited.

(E) Cathodoluminescence imaging of the phase transition from LT to HT phase in $CsPbIBr_2$ nanowires with three different temperature populations and their phase propagation rates.[44]

(F) Arrhenius plot of experimental and MD simulation data for the phase propagation kinetics in the phase transition of $CsPbIBr_2$ nanowires.[44] Copyright 2020 with permission from Elsevier.

sandwiching the metal halide framework "flatten" the interface, and the resulting well-ordered interface has a lower vacancy concentration, both of which contribute to a stabilized interface at ambient and elevated temperatures. The idea that structural ordering can stabilize the interfacial composition gradient provides a new method to make better and long-lasting heterostructures. Furthermore, the atomically sharp interface will be of interest for new fundamental studies.

Phase transition kinetics

Phase transitions in halide perovskites can introduce another approach to design different structures or heterostructures. There are various structural phases related

to the perovskite structure, resulting in diverse transitions between them.[58] Among all the phase transitions in halide perovskites, the transition between the high-temperature (HT) perovskite phase and the low-temperature (LT) non-perovskite phase has received much attention since it dramatically influences the optoelectronic performance of perovskite-based devices, such as solar cells. Taking $CsPbI_3$ as a model example, the HT phase is preferred over the LT phase because of its suitable, direct band gap for photovoltaics, but it is thermodynamically unstable at room temperature and under ambient conditions. The phase transition between HT and LT phases can be triggered by various external stimuli, including temperature, moisture or other polar solvents, and light.[17,25,58–60] By thermal heating, the LT phase can be transformed into HT phase. This thermally driven phase transition from LT phase to HT phase in $CsPbBr_2I$ has been monitored and quantified via *in situ* cathodoluminescence microscopy (Figures 3E and 3F).[44] In combination with MD simulations, it is revealed that the transformation does not follow a simple martensitic mechanism but proceeds despite a substantial energy barrier via ion diffusion through a liquid-like interface between the two structures. The reverse transition from HT-to-LT is also of fundamental interest because this transition direction accounts for one of the degradation mechanisms of perovskite-based devices. Suggested by MD simulations, the absorbed H_2O thin layer facilitates the HT-to-LT transition by enhancing vacancy formation in $CsPbI_3$, due to the large solvation enthalpy and the low vacancy formation energy of halide anions.[17] A recent study into the kinetics of the moisture-induced HT-to-LT phase transition in $CsPbI_3$ has been able to separate the nucleation and growth steps and revealed a nucleation-limited transformation process.[60] The nucleation rate of LT $CsPbI_3$ increases exponentially with rising relative humidity (RH) level, because higher RH creates more surface halide vacancies that lead to lower nucleation barriers. Based on the understanding of these physical mechanisms, structural control of halide perovskites can thus be fully implemented for synthesis and engineering.

The fundamental studies of phase transition kinetics and how environmental factors facilitate phase instability have paved the way for better photovoltaic design. For example, the reversible phase transition between the HT and LT phases with triggering factors such as heating or moisture is utilized to create thermochromic solar cells (Figure 1H).[17] The softness of the perovskite lattice has again become a pivotal point in this reconfigurable and reversible phase transition device. Because of the dynamic ionic framework of halide perovskites, these thermochromic perovskite photovoltaic cells can transform between the two phases for more than 40 cycles without compromising performance. The direct and smaller band gap of the HT phase ensures higher light absorption in the visible spectrum, while the LT phase has an indirect and larger band gap and therefore much larger optical transmission. The reversible transition between these two optically distinct phases enables the concept of a thermochromic smart window, which can change from transparent to dark and simultaneously transforms sunlight into electricity when the temperature is high.

PROBLEMS: MECHANISM, INTERFACE, AND STABILITY

Growth mechanism and design principles

The synthetic tunability of halide perovskites is a fascinating phenomenon, but lingering questions regarding the growth mechanism remain unanswered. The fast nucleation rate, low-temperature reaction kinetics, and complicated byproducts make *in situ* or *ex situ* studies challenging. Debate around the growth mechanism is due to the fact that halide perovskite nanocrystals are so easily synthesized such

that every lab has their own preferred recipe, which makes it difficult to unravel the underlying growth mechanism. A consensus on the reaction mechanism can only be made when a coherent synthetic framework is shared. Here, we present some examples of the controversial understandings of the synthetic aspects of halide perovskite nanocrystals.

Early studies on the synthesis of $CsPbX_3$ nanocrystals typically report the structure to be cubic, α phase.[5] However, later investigations using synchrotron X-ray scattering techniques have revealed that $CsPbBr_3$ quantum dots actually adopt the orthorhombic, γ phase.[61,62] Low-dose HRTEM techniques have also discovered local octahedral distortion inside the domains of individual nanoparticles (Figure 1G).[16] The Scherrer line broadening and weak intensities of characteristic γ phase peaks have contributed to the misinterpretation of XRD data, and the uncontrolled electron doses in typical TEM acquisitions also limit reliable contrast interpretation of TEM results. In addition to the cubic-orthorhombic ambiguity, there are reports on local structural disorder and line or planar defects, such as twin boundaries.[63,64] To achieve better synthetic control of perovskite nanocrystals, resolving the atomic level structural imperfections is critical.

Another lingering question regarding the growth mechanism of halide perovskites is how the cubic or quasi-cubic halide perovskite lattice can lead to symmetry-broken anisotropic growth of non-cubic morphologies, such as nanowires and nanoplates. Some reports have hinted at oriented attachment as a nanowire growth mechanism,[65] but other reports on the systematic monitoring of nanowire growth have shown linear growth kinetics, which cannot be explained by oriented attachment.[21] Thermodynamic considerations are employed to explain the growth mechanism of lower-symmetry products,[66,67] but microscopic investigations as to how precursor transformation kinetics and ligand binding lead to symmetry breaking are still missing.

For the CVT growth for halide perovskites, the control of morphology, dimensionality, and size of nanoscale/microscale single crystals often depends on the interplay between growth temperature, time, pressure, flow rate, and substrate material or its crystal structure.[68,69] A systematic understanding of the underlying relationship between these factors and the resulting crystals has yet to be established. Current studies have shed some light on how substrates play a role in guiding the growth of halide perovskites. For example, whether the substrate surface is highly crystalline (e.g., mica, sapphire, $SrTiO_3$, etc.)[26,28,29,35] or amorphous (Si wafer with native oxide)[27] often determines the epitaxial nature and thus the homogeneity of crystal morphologies. For highly crystalline substrates, it has been shown that the crystal symmetry of a substrate or different crystal planes can guide the growth of halide perovskite crystals.[26,35] A close look at the epitaxial interface is necessary to understand how the epitaxial growth occurs from the atomic scale and is governed by the interlayer interactions.[69–71] However, such experiments are challenging due to the difficulty in creating a thin cross-section sample suitable for HRTEM studies. Focused ion beam milling combined with the lift-out technique[72] is the typical way to prepare such cross-sections, but it has only shown limited success for halide perovskites, partially due to the damage induced by the high-energy Ga ion beam that is typically used. The electron beam damage to thin perovskite cross-sections during TEM imaging is another concern.[73,74]

Interfacial engineering

In the "past" and "present" sections, we have introduced various post-synthetic tools to create halide perovskite heterostructures. However, creating an interface

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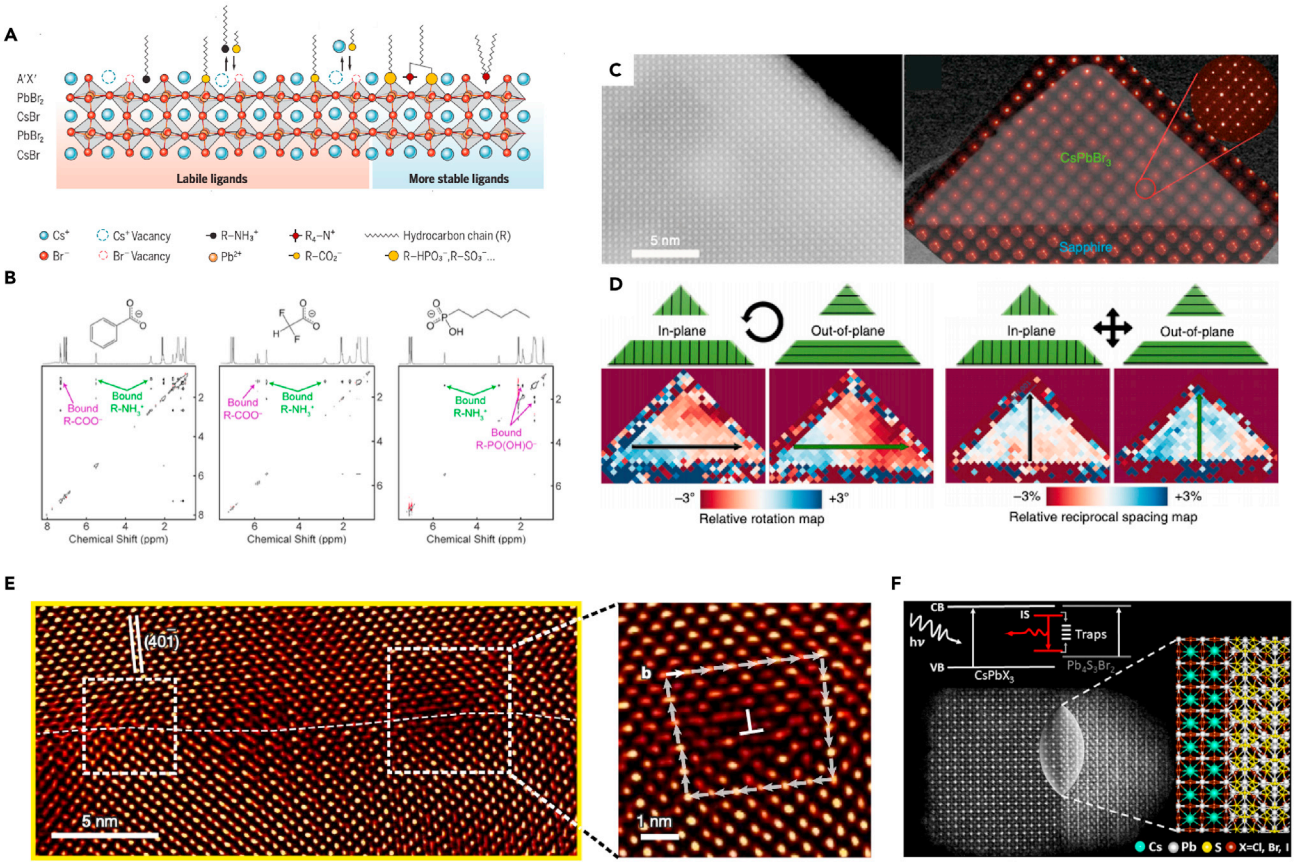

Figure 4. Ligand chemistry and interfacial engineering

(A) Schematics to show different types of ligand bonding and dynamics on the surface of $CsPbBr_3$ nanocrystals.[50] Copyright 2019 American Association for the Advancement of Science.

(B) 2D NOESY as a tool to investigate the ligand binding dynamics of $CsPbBr_3$ nanocrystals.[47] Copyright 2018 American Chemical Society.

(C and D) STEM image and nanobeam scanning electron diffraction analysis of a single-crystal $CsPbBr_3$ nanowire grown on a sapphire substrate, and the in-plane and out-of-plane relative reciprocal-lattice rotation map and relative reciprocal-lattice spacing map for the nanowire cross-section.[78] Copyright 2020 Springer Nature.

(E) Fourier-filtered and magnified aberration-corrected HRTEM images of the $(2T)_2PbI_4$-$(2T)_2PbBr_4$ heterostructure showing the epitaxial interface, with the edge dislocations highlighted.[39] Copyright 2020 with permission from Springer Nature.

(F) High-resolution HAADF-STEM image of a single $CsPbBr_3$-$Pb_4S_3Br_2$ heterostructure with a clear interface.[75] Copyright 2021 American Chemical Society.

with another material of a different crystal structure is still a challenging task. In this subsection, we discuss the remaining problems of interfacial engineering of halide perovskite heterostructures.

Even though there has been a growing number of reports on the heterogeneous, core/shell structures of halide perovskites, an atomically defined, epitaxially grown core/shell interface between halide perovskite and another covalent semiconductor has not been realized.[75–77] The core/shell geometry, compared with other heterostructures such as the Janus geometry, has the advantage of protecting the halide perovskite from the attack of polar solvents or humid environments. Resolving the atomic structure of the interface is key to proving whether the heterogeneous interface is coherent or not and demonstrating how interfacial defects, such as dislocations, are distributed (Figures 4E and 4F).[75] The high crystallinity of the shell materials, rather than porous or random deposition of the shell materials, is also

essential for compact protection from the environment. Selection of a suitable shell material to modulate or improve the electronic properties of the core material is another consideration so that the shelling of halide perovskites will not compromise their excellent optical efficiency.

Epitaxial growth of halide perovskite on a substrate is an important step toward strain engineering, large-scale patterning, and photonic or electrical applications. Epitaxy is defined as a type of growth in which the atoms of the growing layer mimic the atomic arrangement of the crystalline substrate,[69] leading to a coherent lattice-matched interface. A control of the hetero-growth of halide perovskite on another material with epitaxial relations is favorable, and a solution could be found based on a deeper fundamental understanding of the nucleation, growth, and interface chemistry of the two related materials. For vapor-phase synthesis techniques, such as CVT, the choice of substrate plays a vital role in epitaxial growth. A single-crystalline substrate with crystallographic relation matched with or similar to the perovskite structure may directly lead to the epitaxial growth of halide perovskite layers.[26,35] A coherent epitaxial growth entails a strained interface, whose presence can influence the optoelectrical properties, thermodynamic stability, and large-scale growth mechanism of the resulting perovskite film. Research has shown several examples of how the substrate surface symmetry can guide the growth of halide perovskites with controlled morphologies, orientations, and patterns, which largely depends on the strains developed near the perovskite-substrate interface due to lattice mismatch. Although the community has recently explored the atomic structure and strain distribution of epitaxial interfaces (Figures 4C and 4D),[78] due to the limited substrate materials the community has studied, the control of strain build up and distribution is still not well explored.

Engineering halide perovskite growth and transformation may also pave ways for designing perovskite-based integrated photonics. Photonic integrated circuits (PIC) on silicon (Si) are the most common platforms because the cost and performance of Si electronics make it the most favorable host material.[79–81] Si also has the advantage of high crystal quality and easy integration into electronic circuits. Analogous to electronic circuits, the essential building blocks of PIC may include optical amplifiers, phase shifters, polarization converters, and waveguides.[82] Therefore, integration of all these components critically depends on the growth and engineering of multiple types of semiconductors on Si. However, the material incompatibility of Si with traditional semiconductors (e.g., III–V compounds) has been the greatest barrier to further development of Si-integrated photonics.[79] Halide perovskites easily crystallize and grow on various substrates including Si, so patterned perovskite arrays on Si are promising units as emitters or lasers in a functional PIC.[82] Although there are some preliminary synthetic efforts that demonstrate the capability of patterned growth of on-chip halide perovskite light sources, their full integration with Si and other functional units (e.g., complementary metal oxide semiconductors, or CMOS) has not yet been explored. In addition, continuous-wave operation via optical or electrical pumping requires a better understanding of the lasing behaviors and the stability of halide perovskites.[83]

The difficulties associated with properly interfacing halide perovskites with other materials have a deep origin in the structural uniqueness of halide perovskites.[8,76,77] The drastic difference in the bonding types between halide perovskites and typical covalent semiconductors results in challenging interfacial engineering. The apparent lattice match is no longer a good criterion for selecting shell material candidates; coordination environments, molecular orbital hybridization, turning

terminating halides at the perovskite surface into bridging halide, etc., are all factors to be considered. In addition to the structural consideration, the synthetic considerations, such as reaction kinetics, ligand selection in solution-phase synthesis, thermal expansion management in vapor phase synthesis, and relative stability between halide perovskites and the interfacing materials are also crucial in designing a good heterogeneous structure.

Environmental susceptibility and *operando* stability

A comprehensive evaluation of synthesis should concern not only the quality of its end products but also the completeness of the synthetic "ecosystem," which consists of reaction reproducibility, sample integrity during characterization, and long-term performance during normal operation. The facile synthesis of halide perovskites yields nanostructures with immediate excellent structural and optical properties, but the end products often suffer from various stability problems, which limit the application of the end products in different environmental conditions. We divide the stability problems into two categories: one is related to the instability of halide perovskites against environmental factors; the other is related to their instability under *operando* conditions.

In the first category, humidity, polar solvents, and electron beams are the main sources that induce the environmental instability of halide perovskite nanostructures. Ambient humidity or polar solvents can trigger the phase transition of $CsPbI_3$ from HT phase to LT phase.[17,84] In the solution phase, the presence of polar molecules is one of the key factors that contributes to nanocrystal degradation. Ironically, the major polar molecules in solution are actually the capping ligands.[85] A subtle balance between protection and destruction is critical when selecting the capping ligands, as an excess of ligands leads to the structural evolution or degradation of halide perovskites, but inadequate protection by capping ligands results in the coalescence of nanocrystals. This issue of coalescence is further exacerbated in assembled nanocrystal superlattices, which have also been reported to suffer long-term stability problems even under vacuum.[21,47] The combination of these stability issues further complicates fundamental studies of perovskite nanocrystal superlattices and solid-state applications of perovskite nanocrystals.

In addition to their susceptibility to chemical species, halide perovskites are also subject to damage from electron beams, which are typically used as imaging probes. Even though inorganic halide perovskites can endure electron doses 10 to 100 times higher (accumulated dose ~100–1,000 e/Å^2) than the hybrid version,[86] this beam tolerance is still much lower than a typical dose required for atomic resolution.[16] Electron beam damage and perturbations from strong electron-matter interactions can interfere with the interpretation of observed signals and image contrast. Reliable data interpretation requires scrutiny over the sample integrity during imaging and careful examination of the potential electron-matter interaction.

In the second category, the instability of the active halide perovskite layer in devices under *operando* conditions (e.g., under an applied electric field or light irradiation) also poses concerns related to device performance.[74,87,88] For instance, there are some earlier reports on the anomalous hysteresis in the current-voltage (I-V) characteristics of perovskite solar cells.[89] This was later attributed to the polarization of the perovskite layer induced by halide ion (or vacancy) migration.[90,91] In the previous section, we discussed the low activation energies for ion diffusion in halide perovskites. Such moveable ions would retard the change of charge distribution that contributes to the slow time component appearing in the I-V hysteresis curve, leading to unstable device measurements for perovskite solar cells.[90] Elevated temperature,

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Table 2. Two sides of the same coin: the strengths and shortcomings of the soft lattice of halide perovskites

Soft lattice	Positive side	Negative side
Melting temperature and reaction kinetics	solution processable, capable of low-temperature synthesis	nucleation is too fast to be captured reliably
Reconfigurability and synthetic flexibility	morphology control, easy compositional and structural change, post-synthetic engineering	degradation: environmental instability, long-term operational instability
Structure diversity	large diversity in composition, structure, and morphology	design principle is elusive
Organic-inorganic integration	soft matter properties, superstructures, incorporation with functional organic components	intrinsic thermal instability, ligand desorption, structural disorder
Ion mobility	anion exchange, phase transition	unstable heterostructures, hysteresis under bias

electric fields, and light are known to accelerate anion migration in halide perovskites. In perovskite optoelectronic devices made of mixed-anion halide perovskites, such as $CsPbBr_xI_{3-x}$, heat- or light-enhanced anion diffusivity contributes to phase segregation that separates the mixed-anion composition into bromide-rich and iodide-rich components.[92] Such phenomena severely impact device stability by causing changes in absorption/emission wavelengths and by creating unfavorable carrier distribution or migrations in the halide perovskite layers.

POSSIBILITIES: NEW CONCEPTUAL FRAMEWORKS AND SYNTHETIC DESIGN PRINCIPLES

The dichotomies between structural reconfigurability and instability

In this perspective, we demonstrate that the unique structural properties of halide perovskites have prompted an accelerated advancement of synthesis and device applications. In the "problem" section, we mention that the unique properties of halide perovskites also result in certain difficulties in engineering, synthesizing, and stabilizing these materials. We summarize the key characteristics of halide perovskites in Table 2, where we highlight the well-known excellent properties of halide perovskites as well as the associated problems. The dichotomies enumerated here should be acknowledged, because appreciating only the bright side of halide perovskites but avoiding their potential limitations or focusing only on the shortcomings without considering their structural origin cannot do justice to the complexity of these problems. These diametrically opposed properties are two sides of the same coin. In this section, we address how the dichotomies can be reconciled and provide new possibilities in the synthesis of halide perovskite nanostructures. The new conceptual scheme (Figure 5) provided in this section highlights the facts that (1) halide perovskites have unique structural properties that are not properly defined by conventional terms, so a new theoretical framework is needed to describe the structure and properties of the material; (2) characterization is an integral component in the synthesis, so *in situ* platforms that monitor, assess, and provide feedback to the synthetic processes are important tools to understand the growth and degradation mechanisms and to develop new synthetic methods; (3) new synthetic systems and workflows, such as high-throughput synthesis and machine learning algorithms, are emerging techniques that can facilitate the development of new synthetic methods and can tackle stability problems from new perspectives; and (4) a combination of theoretical simulation and experimental data is the key to the construction of a holistic picture of halide perovskites.

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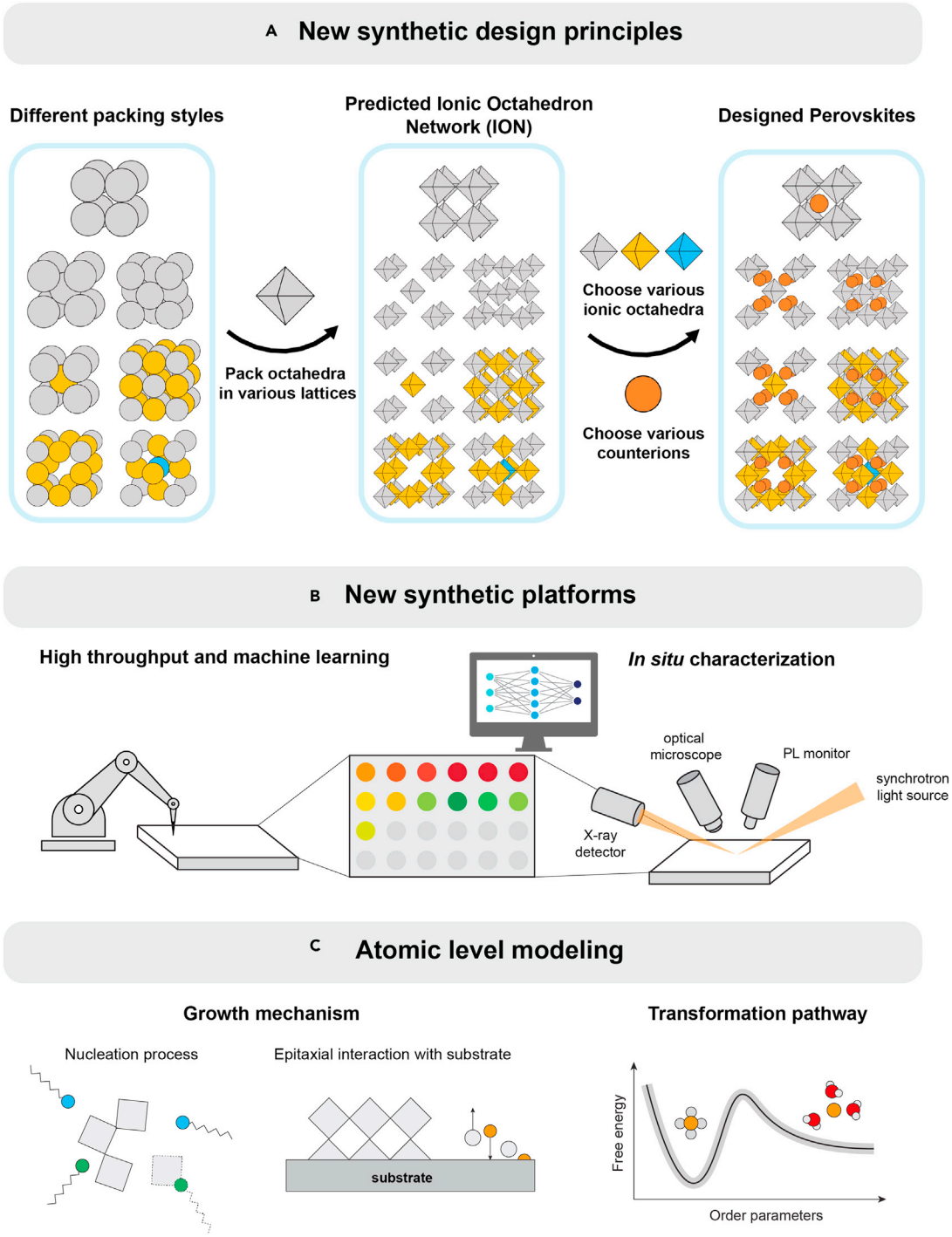

Figure 5. Possibilities of a coherent framework to address the challenges and problems in the synthesis and design of perovskite nanostructures

(A) The concept of ionic octahedron units (IOUs) as building blocks for construct a library of different perovskite-derived ionic octahedron networks (IONs).

(B) Synthetic platforms that coherently comprise high-throughput synthesis, machine learning, and *in situ* characterization tools to facilitate the exploration of new synthetic spaces.

(C) Theoretical modeling to investigate the growth mechanism and transformation pathways of perovskite structures.

Beyond the definition of crystallinity

Appreciating the reconfigurability of halide perovskite lattices necessitates discussion of a new language to describe this material. To account for the liquid-like dynamic disorder, that is, in high-symmetry phases of halide perovskites, there could be local disorder that is not well resolved through typical structural characterization (such as single-crystal X-ray diffraction), a polymorphism explanation to include local low-symmetry motifs has been proposed.[93] However, this description is still largely static and does not fully appreciate the dynamic lattice that has been observed through light scattering spectroscopy and inelastic neutron scattering experiments.[42] A coherent structural description to include both local distortion and temporal phonon fluctuation, and their implications in the electronic properties of halide perovskites, would be a future direction for theoretical investigation.

The interfacial or local inhomogeneity not only challenges the traditional definition of a "crystalline" material but also impacts the efficacy of synthetic platforms. Defects (either intrinsic due to vacancies or extrinsic due to unintended impurities) can dramatically change the optical properties of halide perovskites.[94] Simply excluding the presence of these local inhomogeneities might eliminate the possibilities of utilizing them. Rather, a coherent framework that includes the local structures into the material platform and evaluates their influence is needed. Similarly, organic components are essential to certain halide perovskite structures; therefore, how to holistically do justice to both the inorganic and organic parts is key to the engineering and control of their morphology, properties, and stability.

Manipulations of halide perovskites at the scale of the ionic octahedron unit

One key characteristic of halide perovskites as ionic crystals that is typically overlooked is that the halogen atoms can serve as both terminating and bridging species. A typical ABX_3 perovskite has a 3D-connected framework with all the halogen atoms as bridging halides with a coordination number of 2. On the other hand, halides on the edge layers of 2D Ruddlesden-Popper phases are terminating halides whose coordination number is no longer 2. This non-definitive coordination environment of halides provides the possibility for manipulation of metal halide "molecules,"[95] or, more specifically, the metal halide $[MX_6]^{n-}$ ionic octahedron units (IOUs) with controllable connectivity and packing geometry (Figure 5A).

The $[MX_6]^{n-}$ IOU is considered the basic building block and functional unit of metal halide perovskites.[96] The choice of metal cation in the IOU affects the charge of the IOU and thus the connectivity of these octahedra in the resulting perovskite crystal structure,[97,98] and both the metal cation and the halide anion in the IOU contribute to the electronic structure and optoelectronic properties of the resulting crystal.[99] For example, the "construction" of $[TeCl_6]^{2-}$ IOUs results in unique luminescence properties in their crystal hosts.[100,101] In addition to the choice of metal cations and halide anions, the packing and connectivity of the IOUs will also greatly influence the properties of halide perovskites. Jin and coworkers proposed a new perspective and design principle for halide perovskites, whereby the packing and connectivity of IOUs result in an ionic octahedron network (ION) in the resulting perovskite crystal.[102] By representing each IOU as a super atom/ion, halide perovskites can be described as an extended ION balanced by counter cations. For example, the prototypical $CsPbBr_3$ perovskites can be considered as a simple cubic lattice-based ION balanced by Cs cations. Similarly, the body-centered cubic packing of $[PbBr_6]^{4-}$ IOUs results in the Cs_4PbBr_6 halide perovskite derivative. This design principle allowed for the discovery of a new halide perovskite, $Cs_8\{[InCl_6][AuCl_5][Au_{5/6}In_{1/6}Cl_4]_3\}$, in which three different IOUs self-assemble into a $BaTiO_3$-

type lattice. Other predictions that have not been experimentally realized include new halide perovskite structures based on the CsCl-type ION [$Cs_8M(I)M(III)X_{12}$], ReO_3-type ION [$Cs_8M(I)M(III)_3Cl_{18}$ or $Cs_8M(IV)M(II)_3X_{18}$], and $BaTiO_3$-type ION [$Cs_8M(III)M(III)M(III)_3X_{23}$ or $Cs_8M(IV)M(III)M(III)_3X_{24}$].[102] This design principle based on the ION concept introduces an enormous synthetic space to design new halide perovskite crystal structures through the manipulation of nanoscale IOU building blocks. Moreover, there are further possibilities in the packing of IOUs when other spacers or counterions are introduced within the soft lattice.

High-throughput synthesis

In addition to the fast progress of morphology and (super)structure engineering, high-throughput synthesis and machine learning are emerging techniques to efficiently explore the large synthetic parameter space. Robot-assisted automated synthesis platforms capable of controlling chemical reactions, simultaneous characterization, and ensured reproducibility can greatly facilitate the development of new synthetic methods and the exploration of growth mechanisms.[103] Microfluidics is another high-throughput platform to study a larger parameter space with an accelerated reaction and characterization workflow.[104] Although current high-throughput synthesis has incorporated most optical characterizations, there still exist phase and composition ambiguities by using optical spectroscopy alone. Therefore, given the fast development of this new synthesis tool, a better understanding of the fundamental structural properties and growth mechanism of halide perovskites is only more urgent than ever.

Not surprisingly, the large volume of experimental data generated from high-throughput synthesis requires advanced machine learning algorithms for experimental data recognition and analysis, sample classification, parameter selection, and the prediction of new phases or structures. Consequently, the combination of high-throughput platforms and machine-learning techniques has opened new opportunities that require multidisciplinary contributions from mechanical engineering, electrical engineering, computer science, and, of course, chemical sciences.

Integrating characterization and computation into synthesis

Characterization is an integral part of synthesis. While the structural properties of halide perovskites sometimes elude conventional understanding, the characterization of nanoscale halide perovskites is even more challenging. In the same series of the Pieces Perspectives, Stranks et al.[110] discuss in detail the characterization tools to understand halide perovskites. In this perspective, to address the remaining synthetic problems and to look ahead to new opportunities, we emphasize the integrated role of characterization through the synthetic perspective by noting (1) the structural evolution or fluctuation due to perturbation from a probing light source or electron beam, (2) how to handle the problem of sample integrity during imaging, and (3) the *in situ* tools to monitor the growth kinetics and degradation pathways.

Structural evolution under light excitation is an interesting phenomenon as it reveals the strong light-matter interaction that involves not only electrons but also the ionic lattice framework. Optical Kerr effect measurements on hybrid halide perovskites have revealed liquid-like reorientation motions of the organic cations.[105] In addition, in inorganic halide perovskite nanocrystals, time-resolved X-ray diffraction patterns have revealed reversible structural transitions after photoexcitation.[62] These studies not only demonstrate the dynamical lattice of halide perovskites but also show how the laser source, which is meant to probe the electronic properties, can also induce a structural evolution.

Due to electron beam sensitivity, the sample integrity of halide perovskites throughout the imaging process should be carefully handled. Particularly, management of the electron dose budget during acquisition is an essential step toward reliable low-dose imaging. The recent advancement of fast electron cameras or pixelated detectors also opens new opportunities of electron ptychography, which is a more dose-efficient technique than conventional annular dark-field scanning TEM.[106] Cryo-EM is another tool that can mitigate electron beam damage, especially with new types of rigid TEM grids that minimize sample drifting during low-temperature acquisition.[107]

Better *in situ* characterization designs may help to elucidate the mechanisms of growth, degradation, or structural evolution of halide perovskites under certain environments. Visualizing the growth of halide perovskites may be realized by probing the reaction (from precursors to intermediates to end products) with X-rays, electron beams, or optical tools that can be integrated with the growth apparatus. Early examples include the controllable growth of some oxide materials by using pulsed laser deposition or molecular beam epitaxy, where the growth chamber is coupled with a detector to record high-energy electron diffraction patterns. In halide perovskites, there are also a few demonstrations of using synchrotron X-rays for *in situ* tracking of solution-processed perovskite film growth.[108] However, this method is not quite generalizable as it cannot provide any insights on the growth of perovskite nanoscale or microscale single crystals. If coupled with high-throughput synthetic platforms, *in situ* tools can provide more insights on the reaction pathways and growth mechanisms.[103]

Conceptual or experimental, new possibilities described in this section should be compared with computational investigation. For example, MD simulations have been utilized to elucidate the hybrid nature of halide perovskites and their interfacial stability.[17,39] These aforementioned studies combining experimental and theoretical techniques have provided new insights into stabilizing perovskite nanostructures. Analyzing high-throughput data with computational theories (such as Monte Carlo simulation, MD simulation, or kinetics theories) will also shed light on the reaction mechanisms and degradation processes of perovskite nanocrystals.

Addressing the stability problems with well-defined nanostructures

The synthesis of halide perovskites can be roughly classified in three categories: bulk single crystals or powders, nanostructures, and thin films (or device-level architectures). The first category is mainly focused on exploration of new materials; the second, the focus of this perspective, has drawn researchers' attention due to their unique electronic and structural properties; the third category, however, is the primary focus of halide perovskite research because of its simple integration into device-level architectures for sustainable energy conversion. Although integrating nanostructures with device-level architectures is not new (e.g., quantum dot solar cells and LEDs), fundamental studies of nanoscale perovskites and device-level engineering are typically investigated independently, if not separately. In this subsection, instead of emphasizing the uniqueness of halide perovskite nanostructures, we show that well-defined perovskite nanostructures can provide new opportunities in the design of high-efficiency optoelectronic devices with long-term stability.

In the "present" section, we have shown that the structural properties of halide perovskites can be quantitatively extracted from well-designed nanocrystal platforms. Knowledge gained therefrom can be applied to the design of better optoelectronic devices. For example, vacancy-mediated halide diffusion or segregation, as suggested by the fundamental studies described above, can be suppressed with the

presence of a stable chelating ligand shell, whose design and characterization require an understanding of the basic surface chemistry of nanocrystals. With surface treatment, nanocrystal-based halide perovskite devices have shown color-stable emission under electrical bias with 20.3% external quantum efficiency.[109] This case study is not only an excellent example of the application of nanostructures at the device level but also demonstrates that nanocrystal chemistry (synthetic methods and characterization tools), physical chemistry studies (extraction and understanding of key thermodynamic and structural parameters), and device-level fabrication (interfacial engineering, design of charge transport layers, and deposition techniques) should be studied together to address the remaining problems in the perovskite community (such as structural degradation or *operando* stability).

Understandings of nanoscale objects or phenomena have provided a "local" perspective in the systems engineering of halide perovskite optoelectronics. A coherent framework to address the challenges and problems in the synthesis and design of halide perovskites should integrate this local perspective with higher level knowledge.

The soft lattice imparts synthetic flexibility to halide perovskites but at the same time presents challenges for stability, device integration, and materials characterization. We believe that a better synthetic understanding will shed light on a universal design principle for the next generations of halide perovskite nanostructures that preserves their functional properties but imbues higher stability and complexity for fundamental studies and device applications.

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