Phase Engineering in Quasi-2D Ruddlesden−Popper Perovskites

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ABSTRACT: Quasi-2D Ruddlesden−Popper (RP) halide perovskites have drawn intensive research interest because they possess superior ambient stability while retaining excellent device performance as compared to their pure 2D or 3D counterparts. By phase engineering strategy, quasi-2D perovskites can fall into three types—large-\(n\) 2D perovskite, 2D:3D mixed perovskite, and 3D/2D bilayer perovskite. This Perspective discusses the modulation of phase composition, hierarchical distribution, and crystal orientation in quasi-2D perovskites, aiming to uncover the correlation between morphological structure, band alignment, and charge recombination. A perspective of phase engineering in 2D RP-type perovskite materials is then given toward the concurrent stability and device efficiency.

Owing to their superior ambient stability, two-dimensional (2D) Ruddlesden−Popper (RP) organometallic perovskites have recently attracted rapidly increasing attention. The general chemical formula for 2D RP-type perovskites is \(L_2A_{n-1}B_nX_{3n+1}\), where \(A\) is a conventional monovalent cation (= CH\(_3\)NH\(_3\)+, HC(NH\(_2\))\(_2\)+, Cs\(^+\), etc.) while \(L\) is a larger aromatic or aliphatic alkyammonium organic spacer cation (= 2-phenylethylammonium (PEA), \(n\)-butylammonium (\(n\)-BA), etc.) that tailors the 3D perovskite into layered 2D structures, \(B\) is a divalent metal cation (= Pb\(^{2+}\), Sn\(^{2+}\), Ge\(^{2+}\), Cu\(^{2+}\), etc.), \(X\) is a halide anion (= Cl\(^-\), Br\(^-\), or I\(^-\)), and the variable \(n\) (= 1, 2, 3, 4, ...) represents the number of inorganic layer within each quantum well. As such, 2D perovskites enable one to readily tailor the optical bandgap and absorption by varying either the spacer cation structure or the variable \(n\) while the organic spacer largely increases stability against oxygen and moisture.\(^1\sim^3\)

Recently, a few years have witnessed tremendous development in 2D perovskites-based solar cells. Their power conversion efficiency (PCE) has rapidly increased from \(\sim4\%\)\(^4\sim^5\) in 2014 to 13.7% in 2017 through either optimized fabrication (“hot-casting” technique) or composition engineering (Cs-inclusion method).\(^6\sim^7\) However, such performance is remarkably worse than that of 3D analogues (up to 22.7%),\(^8\) which can be attributed to hindered charge transport by the insulating nature of inserted long organic spacers and random packing of crystals in 2D perovskites. Of particular relevance is that the nominal 2D perovskites are a mixture of phases with different quantum well widths. Yet, there lacks an effective means to regulate the ratio and hierarchical distribution of mixed phases to achieve favorable band alignment and charge transport.

Notably, a multitude of research groups have successfully fabricated 3D/2D perovskite hybrids, resulting in a new era of perovskite research for high-efficiency thin film photovoltaics with superior air stability.\(^9\sim^27\) These dimensionally mix-phased perovskites are denoted as quasi-2D perovskites. By far, as shown in Figure 1, there are mainly three routes to create them: (1) increasing the ratio of spacer cations in the precursor solution, (2) mixing 2D and 3D perovskites in solution, which involves both one-step and two-step processing methods (Figure 1b), and (3) depositing a thin layer of 2D perovskite on top of a 3D perovskite thin film to generate the 3D/2D bilayer structures (Figure 1c).

This Perspective will first present the synthesis, energetic structures, optical properties, and carrier dynamics of quasi-2D perovskites. Next, the three above-mentioned types of quasi-2D perovskites will be discussed and compared. Finally, the outlook of these hybrid perovskites in optoelectronic devices will be given and a critical perspective offered to guide the design of novel perovskite structures.
Varying the Thickness of Inorganic Lattices (n). With the increase of the n value from 1 to ∞, the perovskite structure undergoes dimensional evolution, which transits gradually from pure 2D phases to 3D:2D mixtures and finally 3D perovskites, as schematically shown in Figure 2a. It has been reported that

![Figure 2](image)

**Figure 2.** (a) Schematic of 2D (PEA)_2MA_x−1PbI_3−x+1 perovskite structures with varying n value from 1 to ∞. (b) Device performance and stability variation of PCE with n value. Reprinted with permission from ref 9. Copyright 2016 American Chemical Society.

The structures and properties of perovskites varied with the n value. For example, for the (PEA)_2MA_x−1PbI_3−x+1 perovskite, the formation energy increased with decreasing n value, suggesting enhanced air stability.9 Moreover, the energy bandgaps ($E_g$) increased linearly with decreasing quantum well thickness (i.e., n value), giving $E_g \propto 1/n$ at $n > 2$.[10] Meanwhile, the dielectric constants increased largely with $n$, thus lowering the exciton binding energy ($E_{b}$). Furthermore, structural transformation from the 2D to 3D phase brought about a slightly diminished effective mass of electrons ($m_e$) and holes ($m_h$), indicating that the layer thickness (n) has negligible effect on the mobility of photogenerated carriers. Later, Barea et al. investigated the influence of n values on exciton splitting.[11] It was found that there is no quantum confinement effect in the RP halide perovskites with $n \geq 2$, which can be confirmed by the absence of emission or absorption shifts from UV–vis and electroluminescence spectra. This phenomenon is similar to that of the 3D bulk counterpart so that RP perovskites with $n > 3$ can be effectively applied to solar cells. As a demonstration, (CHMA)_x2(MA)_{1−x}PbI_{3−x+1} based solar cells ($n = 1−5$) were compared for device performance.[12] When $n < 3$, the PCE barely exceeded 0.1% while it increased up to ~4% when $n > 4$. Remarkably, the Etgar group synthesized layered perovskites with very large n values ($n = 40, 50, 60$), which exhibited higher open-circuit voltage ($V_{oc}$) and PCE (~8.5%) than their 3D counterparts.[13] On the other hand, the Sargent group showed that utilization of an allylammonium ligand enabled a narrower distribution of QW widths ($n = 10$), thus creating a flattened energy landscape that led to $\times 1.4$ and $\times 1.9$ longer diffusion lengths for electrons and holes, respectively.[14] In addition, the n value impacts greatly the crystal orientation of 2D perovskites. For instance, the (BA)_2(MA)_{1−x}PbI_{3−x+1} 2D perovskite crystals were preferentially aligned parallel to the substrate when $n = 1$ and turned nearly perpendicular when $n = 4$.[15] In short, when $n$ is small, the ambient stability can be guaranteed in RP perovskites owing to the dominant contribution of hydrophobic spacing cations while the charge carrier transportation is hindered, and vice versa. There is always a trade-off between device performance and stability, as indicated in Figure 2b. It is therefore necessary to determine the optimal n value in RP perovskites to compromise between the efficiency and stability in devices.

**2D:3D Mixed Perovskites.** For the n-modulating strategy, it is however inevitable to generate supersmall-n 2D phases (n < 3) that impede charge/energy transfer processes, even when the starting n value in the precursor solution is very large. This can be compensated by the presence of 3D phases with favorable charge transport, which may be formed via self-assembly to some degree yet in an uncontrollable way. In order to attain a delicate control of 3D phases, several research groups have recently generated devices based on a mixture of 2D and 3D perovskites.[16–20] There are two typical routes toward 2D:3D mixed perovskites. One is a “one-step” method that blends the precursors of 2D and 3D perovskites in solution for spin-coating, while the other is “two-step” deposition that spin-casts the mixed solution of an organic cation (A) and spacer cation (L) on the top of the PbI$_2$ layer. In the former method, the Snaith group added n-BA$^+$ into benchmark 3D perovskites of mixed-cation/halide FA$^+$xBr$_y$I$_{3−x−y}$ based solar cells exhibited a stabilized PCE of ~17.5%. It is interesting to note that the 2D phases tended to intersperse between highly oriented 3D perovskite grains, resulting in suppressed nonradiative charge recombination. This phenomenon was also found in the NH$_2$CH$_2$CH$_2$COOH (termed Ava) spacer dication-incorporated MAPbI$_3$-based quasi-2D perovskite.[17] Zhao et al. recently introduced this Ava dication into a 3D MAPbBr$_3$ perovskite to form NH$_2$CH$_2$CH$_2$COO(CH$_3$NH$_3$)$_2$PbBr$_6$ (Ava$_x$), where the protonated NH$_3^+$ groups displaced the MA$^+$ while the COO$^-$ groups took the place of unoccupied Pb$^{2+}$, thereby promoting the formation of smooth planar films with a notably high PLQY up to ~80%.[18] More recently, they reported another organic spacer, ethylenediamine (EDA)-based quasi-2D perovskites, bearing double active sites.[19] It was found that the addition of EDAPbI$_2$ aided in avoiding the formation of the undesirable nonperovskite $\delta$ phase, which can be attributed to the cross-linking capability of EDA. As a result, the devices based on CsPbI$_3$-0.02EDAPbI$_2$ perovskite yielded a PCE of 11.8% with excellent stability at room temperature for months. On the other hand, Jen and his co-workers for the first time employed two-step deposition to introduce phenylethylammonium iodide (PEAI) into FAPbI$_3$ perovskite and generate quasi-2D FA$_{1−x}$PEA$_x$PbI$_3$ structures.[17] The PEA$^+$ ions around the crystal grain boundaries presented dual functions: (i) tightening the FAPbI$_3$ domains via migration into the FAPbI$_3$ grain boundaries to form organic shells with induced $π−π$ interaction and (ii) raising the phase transition energy and passivating the surface to improve both phase and moisture stability. The resulting quasi-2D perovskite solar cells gave a high PCE of 17.7% with superior phase stability in air.

Morphological randomness of 2D:3D mixed perovskites increases the difficulties of device optimization and bench-to-bench reproducibility.
which displays three possible band structure alignments. It is more likely for those mixed perovskites to exhibit a random distribution of 2D and 3D phases (Figure 3a), which leads to mismatched band alignment and thus unfavorable charge recombination, rather than forms favorably flat or ordered band alignments (Figure 3bc).

3D/2D Bilayer Perovskites. In order to resolve the random band alignment in the 2D:3D mixed perovskites, the 3D/2D bilayer heterojunction structure has received exponentially increasing attention. Such structure can be formed by a “cation exchange” method in solution-cast or thermal evaporation. On the other hand, such heterostructures can be varied by modifying the composition of precursors. For example, the Huang group investigated the chemical reaction mechanism of forming 3D/2D stacking structures. They compared two kinds of precursor solution for “cation exchange”: by means of either BA dissolved in chlorobenzene (CB) or BAl dissolved in isopropyl alcohol (IPA), as shown in eqs 1 and 2, respectively. The resulting 2D perovskites possessed distinctive compositions and phases. Intriguingly, reversible conversions can be obtained by such cation exchange reactions with BAl (3D to 2D) or MAI (2D to 3D) solutions.

\[ 2BA + MAI + MAPbI_3 \rightarrow (BA)_2PbI_4 + 2MAI \]  
\[ 2BAI + nMAPbI_3 \leftrightarrow (BA)_2(MA)_{n-1}Pb_{n+1}I_{3n+1} + MAI \]  

The solar cell applications of such 3D/2D bilayered structures were initiated by the Pablo group. They fabricated 3D/2D bilayer perovskite-based solar cells by a “cation infiltration” method that spin-coated a layer of mixed PEAI:MAI or BAl:MAI in IPA solution on top of the MAPbI_3 layer. As shown in Figure 4a, the partial reorientation of crystallites occurred upon formation of the PEAAMI layer, thereby yielding a PCE of 16.84% in solar cells. The same result of such occurrence was also found in MAPbI_3/(BA)_2(MA)_n-PbI_{n+1} 3D/2D bilayers by the Jin group using steady-state and transient spectroscopic measurements. Multiple perovskite phases were arranged in the sequence order of their \( n \) values along the direction perpendicular to the substrate. Carrier transfer within the unique superstructure occurred most likely from the small- \( n \) to the large- \( n \) phase. Moreover, the optimal alignment of graded energy bands provided a continuous upshift of the LUMO level in the 3D/2D perovskite structure, which facilitated charge transfer from the perovskite to the electron-transfer layer (ETL) and also prevented backflow of electron carriers, thus suppressing both charge recombination and ion migration (Figure 4bc).

Alternately, this bilayer structure has manifested as an effective strategy to fabricate high-quality Pb-free perovskite films for achieving promising photovoltaic performance.

For instance, when a PEAI layer was thermally evaporated onto the FASnI_3 thin film, the oxidation of the Sn^2+ could be effectively avoided even in the absence of reductant additive such as SnF_2 and hydrazine. As a result, the resulting solar cells exhibited a promising PCE of 6.98% with good reproducibility.

Table 1 summarizes the up-to-date device performance of 3D/2D bilayer perovskites-based solar cells. It is worth noting that the most adopted 3D perovskite in Table 1 is MAPbI_3 for which further enhancement of PCEs can be realized by using a mixed cation or halide, similar to the methods used in the pure 3D counterparts. For instance, an ultrahigh PCE up to 18.51% was acquired for \( C_{56}(FA_{0.83}MA_{0.17})_{0.99}Pb(IA_{0.16}Bi_{0.17})_3/PEAIPb_2I_4 \) planar solar cells.

The 3D/2D bilayer perovskite structure appears to be the most viable avenue to significantly improve air stability without notably sacrificing PCEs.
Table 1. Device Performance of 3D/2D Bilayer Perovskites-Based Solar Cells

<table>
<thead>
<tr>
<th>3D/2D bilayer structure</th>
<th>device configuration</th>
<th>J_sc (mA/cm²)</th>
<th>V_oc (V)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPbI_3/(PEA)_2PbI_4</td>
<td>FTO/NITO/perovskite/PCBM/PN4N/Ag</td>
<td>21.80</td>
<td>1.17</td>
<td>0.78</td>
<td>19.89</td>
<td>60%/30 d, RH 20–30%</td>
</tr>
<tr>
<td>MAPbI_3/PEA_MaPbI_3o or BA_MaPbI_3o</td>
<td>FTO/c-TiO_2/ perovskite/spiro-OMeTAD/Au</td>
<td>18.63</td>
<td>1.08</td>
<td>0.73</td>
<td>14.94</td>
<td>76%/19 d, RH 75%</td>
</tr>
<tr>
<td>MAPbI_3/(BA)_2PbI_4 or (BA)_2(MA)_3PbI_3</td>
<td>ITO/PTAA/perovskite/PCBM/Cao/ BCP/Cu</td>
<td>16.56</td>
<td>1.08</td>
<td>0.62</td>
<td>11.49</td>
<td></td>
</tr>
<tr>
<td>C_60(FA)2(MA)3PbI3/FA EA2PbI_4</td>
<td>FTO/c-TiO_2/m-TiO_2 /perovskite/spiro-OMeTAD/Au</td>
<td>22.49</td>
<td>1.11</td>
<td>0.78</td>
<td>19.56</td>
<td>96.5%/100 h</td>
</tr>
<tr>
<td>FASNl3/(PEA,FA)SnI_3</td>
<td>ITO/PEDOT:PSS/perovskite/Cao/ BCP/Ag</td>
<td>22.59</td>
<td>1.09</td>
<td>0.77</td>
<td>18.85</td>
<td>88.2%/heat for 100 h</td>
</tr>
<tr>
<td></td>
<td></td>
<td>22.89</td>
<td>1.11</td>
<td>0.73</td>
<td>18.51</td>
<td>94%/1000 h, RH 60 ± 10%</td>
</tr>
</tbody>
</table>

Note that J_sc is the short-circuit current density, V_oc is the open-circuit voltage, and FF is the fill factor.


