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Review

Halide Perovskites Multifunctional Property: Coordination Engineering, Coordination Chemistry, Electronic Interactions and Energy Applications beyond Photovoltaic

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Abstract: Halide perovskite materials gain enormous attention for their semiconducting properties, higher power conversion efficiency and potential applications in a wide range field of studies along with their two key limitations: stability and toxicity. In spite of great progress made on the halide perovskites and many promising research developments, overcoming these limitations is not realized yet. Therefore, coordination engineering of new framework for obtaining alternative new halide perovskite materials and fundamental understanding of the coordination chemistry and electronic interactions forming the structure of these newly engineered halide perovskite materials *might be one way* in order to overcome the issues related to both stability and toxicity. In this review, the current development of halide perovskite families, both lead halide perovskites and lead free halide perovskites followed by coordination engineering of the new frameworks to engineer new halide perovskite materials are reviewed comprehensively. Moreover, all the concerns of the fundamental ideas of coordination chemistry and electronic interactions that are keys in forming the halide perovskite structures are discussed in detail and form the main aim of this review. We also discussed recent potential energy applications beyond photovoltaic and this review has completed with an essential and open question: '*what could happen in the future of halide perovskites?*' in order to excite commercial enterprises and research institutions again as well as to get motivating new predictions on the future continuity of this field.

Keywords: coordination chemistry; coordination engineering; electronic interactions

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1. Background

Photovoltaic devices based on hybrid halide perovskites, specifically $(CH_3NH_3)PbI_3$, are the subject of current studies because of their higher efficiencies and simplicity of production.[1,2] From the time when their pioneering from 2009[3], $CH_3NH_3PbI_3$ perovskite materials have fascinated substantial concentration owing to their potential applications in economic power conversion photovoltaic. Currently, solar cell device based on the hybrid organic-inorganic halide perovskites have achieved power conversion efficiency of 29.15% (www.nrel.gov),[4] which is the quickest-growing photovoltaic field up to now.[5] This is recorded as greater than nine-fold plus step-up in cell efficiency within seven years[6] and the device has theoretical maximum beyond the 30% efficiency record.[7] Its hypothetical limit is superior than 30% and this could hammer the competence of silicon, the hypothetical limit of which is bounded to 27%, and reasonably and nearly bounded to ~25%.[8] Researchers are already stated peroveskite solar cell can reach efficiency of 45% (https://www.ossila.com/pages/perovskite-solar-cells-vs-silicon-solar-cells#:~:text=Researchers%20Break%20the%2030%25%20Efficiency%20Barrier&text=According%20to%20Stefaan%20De%20Wolf,reach%20efficiencies%20of%20around%2045%25.). Regardless of this promising efficiency, there are two key challenges for real applications of these types of solar cells: the long—term stability[9] and toxicity[10,11] during large scale production. Different research groups have been investigating to disclose the reasons for stability challenges such as degradation of the organic part i.e. sensitivity of methylamine group and/or its derivative to the ambient environment.[9] In addition to this, it is important to study if any contributions to high power conversion efficiency and to many applications from the bonding and coordination chemistry of the constituent atoms as well as coordination engineering of the structure.[12–17] It is highly essential to know whether the electrostatic energy is essentially liable for the stability of halide perovskites or the electron-electron interaction contributing to the stability and more to the electrical properties of such compounds.

The great halide perovskite material with suitable electronic and optical properties for various applications of photovoltaic and beyond photovoltaic is $CH_3NH_3PbI_3$ perovskite.[18–21] But, the toxicity of lead atom and its environmental impact during mass production metal and waste disposals become challenging. The difficulty for removal of the toxic lead atom is due to the unsuccessful replacement of the toxic lead metal atom using other environmentally friendly metal atoms. Furthermore, why lead atom cannot be replaced and why the produced lead free perovskite materials could not be achieved the required properties and the performance like the lead halide perovskite materials become an ambiguous question. Is there any special behavior of this lead metal atom over the other post transition metal atoms such as Sn, In, Ge, Sb Bi and others? On the other way, does lead atom have special character of coordination engineering in forming the structure of the $CH_3NH_3PbX_3$ so that lead halide perovskites achieve suitable electronic and optical properties in order to realize their current efficiency? How are the special bonding characters of the halide perovskite complex holding the structure, electronegativity properties of the constituent atoms and electronic interactions of the constituent atoms as well as their contribution expressed?

Although some reviews have been reported,[12,22–25] nowadays, the coordination chemistry and coordination engineering of halide perovskites (both the hybrid organic-inorganic halide perovskites and fully inorganic halide perovskites) become more essential to understand. Similarly, understanding the electronic interactions forming the structure of halide perovskites should get more focus. Unless all these worries get solutions, there will no guarantee to realize the currently confirmed and promising application as well as the future of these halide perovskites materials. For this reason, the aspiration of this article is broadly organizing the recent information about the families of halide perovskites; the coordination engineering; coordination chemistry and electronic interactions forming the structure of halide perovskites. Subsequently, energy applications of halide perovskite beyond photovoltaic such as laser, light emitting devices, photodetectors and efficient nonlinear emission sources, CO_2 reduction and photocatalysis processes such as solar water splitting and HX splitting are reviewed thoroughly. Also, the purpose of this review is to share current status focusing on *what will be the future of halide perovskite materials with wide range applications.* Furthermore, its scope is to review the current issues on the coordination engineering and coordination chemistry of halide perovskites; electronic interactions that help form halide perovskites structure followed by their energy applications beyond photovoltaic in order to assist the industries and scientific community. The *future direction of halide perovskite materials and a concluding remark* are developed to address the major issues into the scientific community and to help readers improve their understanding on this perovskite field.

Finally, the organization of this review is completed with an open question to the scientific community and commercial enterprises: *what will be the future of these materials?* Their instability and toxicity create strong doubt that leads to the open question: *will their commercialization and mass production successful in the future with the expected performance or not?* Based on this essential information, a critical conclusion is drawn.

2. Halide Perovskites

Halide perovsite materials have been revolutionizing the area of photovoltaic with remarkable efficiency and this time its diversity with many perovskite derivative species become very common for researchers. In brief, those currently reported families and list of halide perovskite derivatives as well as the research development and expansion are summarized in Scheme 1 and Table 1.

Scheme 1. Families of halide perovskites: Research development and expansion.

Table 1. Currently reported families of halide perovskites.

No.	Hybrid organic inorganic halide perovskite	Inorganic halide perovskites
1	$MAPbX_3$[26,27]	$Rb_3Sb_2I_9$[28]
2	$FAPbX_3$[29,30]	$Cs_3Sb_2I_9$[31]
3	$MASnX_3$[32]	$Rb_6Pb_5Br_{16}$[33]
4	$FASnX_3$[34,35]	$Rb_6Pb_5I_{16}$[33]
5	$MA_xFA_{1\_x}PbI_3$[36]	$CsRbPb_2I_6$
6	$FA_{1-x}Cs_xPbI_3$[37]	Cs_2SnI_6[38]
7	$MA_{1-x}FA_xGeI_3$[39]	$Cs_2TiI_xBr_{6-x}$[40]
8	$MAGeX_3$[41]	$Cs_2InBiCl_6$[42]
9	$FAGeI_3$[43]	$Cs_2InSbCl_6$[42]
10	$C(NH_2)_3GeI_3$[43]	Cs_2TiX_6[44]
11	MAPbxSn1-xBr3[45]	$Rb_2CuInCl_6$[46]
12	$MAPb_{1-x}In_xI_3Cl_x$[47]	$Rb_2AgInBr_6$[48]
13	$FA_{0.8}Cs_{0.2}SnI_3$[49]	$Cs_2BiAgCl_6$[50]
14	$(PEA)_2(FA)_8Sn_9I_{28}$[51]	$Cs_2AgBiBr_6$[52,53]
15	$(BA)_2(MA)_3Sn_4I_{13}$[54]	$Cs_2AgInBr_6$[55]
16	$(FA)_x(MA)_{1-x}SnX_3$[56]	In_2TiX_6[57]
17	$(CH_3)_3NHGeI_3$[43]	K_2TiX_6[58]
18	$CH_3C(NH_2)_2GeI_3$[43]	$Cs_3Bi_2I_9$[59]
19	$C_5H_6NBiI_4$[60]	$CsPbX_3$[61]

20	$(H_3NC_6H_{12}NH_3)BiI_5$[62]	$RbPbX_3$[63]
21	$MA_3Sb_2I_9$[64]	$Cs_{1-x}Rb_xPbX_3$[65]
22	$(FA)_2BiCuI_6$[66]	$CsSnX_3$[67]
23	$(NH_4)_3Sb_2$I9[49]	H_3SPbX_3[68]
24	$HC(NH_2)_2PbI_3$[69]	$CsGeI_3$[70]
25	$(CH_3NH_3)_{1-x}(HC(NH_2)_2)_xPbI_3$[71]	Tl_2TiX_6[72]
26	$(HC(NH_2)_2)_{0.9}Cs_{0.1}PbI_3$[73]	$CuPbX_3$[74]
27	$[HC(NH_2)_2]x[CH_3NH_3]_{1-x}PbI_3$[75]	$AgPbX_3$[74]

Ordinarily, halide perovskite sensitizers depend on the 3D structure with universal recipe AMX_3, where X = Cl−, Br−, I−; A is $CH_3NH_3^+$ (MA) or $HC(NH_2)_2^+$ (FA); and M is Sn^{2+} or Pb^{2+}. The 3D organization is a progression of corner-sharing MX_6 octahedra involving the cubohoctahedral cavities, keeping up electroneutrality of the framework. Along these lines, because of their tunability properties and probability of different substitutions, different sorts of halide perovskites have been building, which is the focal point of the accompanying subsections. Following the announced performance of 3.8% (2009),[3] perovskite solar cells have risen to achieve performance beyond 22.1% in 2016[76] and then 29.15% obtained from monolithic tandem peroveskite solar cell.[4] With such witnessed performance accomplished by straightforward construction forms, these devices are likewise extremely encouraging for supplementing silicon solar cells in a couple arrangements.

2.1. $HC(NH_2)_2PbI_3$ and Its Derivatives

Among halide perovskite, $CH_3NH_3PbI_3$ and $HC(NH_2)_2PbI_3$ are right now the hero hybrid organic-inorganic halide perovskite materials with ~22.1% record efficiencies. The larger size of $HC(NH_2)_2^+$ results in smaller bandgap compared to the smaller size of $CH_3NH_3^+$, the reason is not known. Normally, when the R-group (carbon chain) increases, the bandgap becomes increased and this leads to discourage achieving higher efficiency but encourages achieving better stability. It is pondering that the utilization of $HC(NH_2)_2^+$ expands proficiency and predominant photostability,[77–83] however, bring down dampness stability[84] of halide perovskites contrasted with $CH_3NH_3^+$. Flimsiness of dark perovskite, $HC(NH_2)_2PbI_3$, is expected to either precariousness of the polar formamidinium itself in nearness of water. Notwithstanding its dampness insecurity, $HC(NH_2)_2PbI_3$ displays sudden concealment of photovoltaic impact as the framework experiences cubic-to-hexagonal progress, after cooling.

2.2. $(CH_3NH_3)x(HC(NH_2)_2)_{1-x}PbI_3$ Perovskite

The paired cation perovskite of $(CH_3NH_3)x(HC(NH_2)_2)_{1-x}PbI_3$ was primary accounted for by Gr¨atzel.[85] To acquire a high caliber and smooth halide perovskite film, this blended perovskite $(CH_3NH_3)_x(HC(NH_2)_2)_{1-x}PbI_3$ was prepared by means of a successive affirmation strategy by plunging PbI_2 in CH_3NH_3I + $HC(NH_2)_2I$ blended arrangement.

2.3. $(HC(NH_2)_2)_{1-x}Cs_xPbI_3$ Perovskites

In order to improve photo and dampness dependability, $(HC(NH_2)_2)_{0.9}Cs_{0.1}PbI_3$ has been accounted for as an elective light safeguard to $CH_3NH_3PbI_3$ and $HC(NH_2)_2PbI_3$.[86] $(HC(NH_2)_2)_{0.9}Cs_{0.1}PbI_3$ perovskite was shaped by means of Lewis base adduct of PbI_2.[87] Optoelectronic properties and photovoltaic execution of Cs-joined $HC(NH_2)_2PbI_3$ were contrasted and those of flawless $HC(NH_2)_2PbI_3$. An efficiency of 19.0% estimated by invert sweep and normal efficiency of 16.5% as of forward output exhibited from $(HC(NH_2)_2)_{0.9}Cs_{0.1}PbI_3$ film in planar structure.[86] More critically, it has been discovered that steadiness of $(HC(NH_2)_2)_{0.9}Cs_{0.1}PbI_3$ film against the light and humidity was enhanced contrasted with $HC(NH_2)_2PbI_3$ film. Improved photo and dampness security of hybridized Cs with $HC(NH_2)_2PbI_3$ is begun from contracting of the cubo-octahedral volume and increment in the concoction association among $HC(NH_2)_2^+$ and I.[88] Li et al. detailed that blending Cs with $HC(NH_2)_2^+$ generously brought down the change in temperature from

165 °C to room temperature. By alloying the $CsPbI_3$, the resistance factor of the perovskite is tuned and the diminishing in stage progress temperature results from the adjustment of the perovskite structure.[89]

2.4. The Difficulty of Replacing Lead Atom by Other Metals

The essential inquiry with respect to lead free materials is the reason lead is so difficult to supplant, to which there is no simple answer. Fundamentally the properties for a B-Site particle are:

a) Ionic radius: best outlined by the tolerance factor: Replacing the toxic Pb in perovskite crystals needs an atom with similar size. The excellent performance of Pb-based perovskites is mainly due to high structural symmetry and strong antibonding coupling between Pb and I.

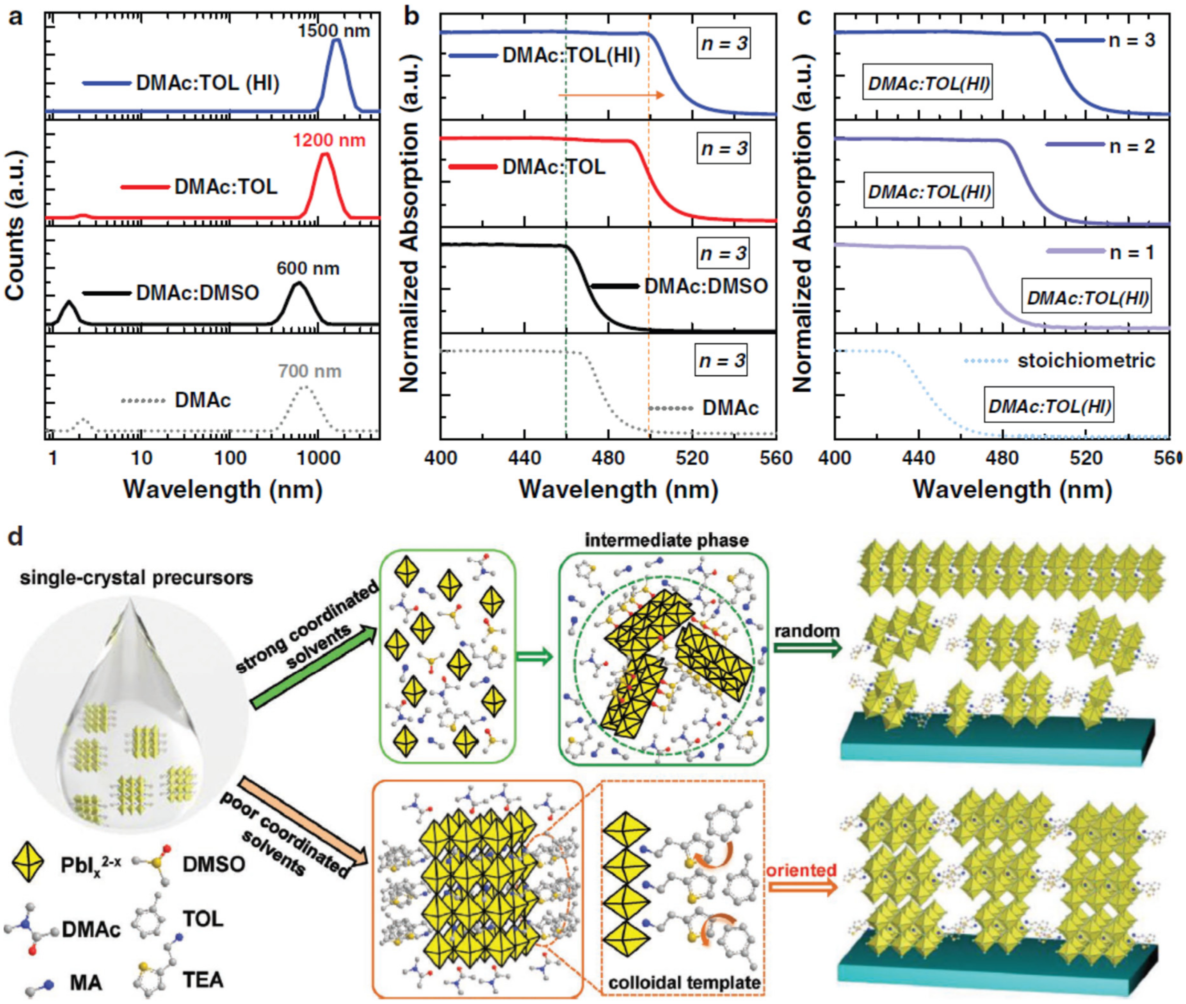
b) High polarizability: lead (II) is considered a softer or borderline hard/soft cation, has plarizable outer electrons, large size, low electronegative and should interact most strongly' with donor types. Typically a soft cation will covalently bond with a soft donor atom which has low electronegativity, highly polarizable low-lying empty orbitals and is easily oxidized, and a hard cation will form an ionic bond with a donor atom which has high electronegativity, low polarizability, and high energy empty orbitals and is hard to oxidize.

c) Valence: a B site atom has in a perfect world a 2+ valence, different configurations are conceivable, and however, they require remuneration to accomplish charge neutrality. Lead (II) has stable oxidation state of +2 with coordination number of 6. All six Pb^{II}-X bonds of the halogen ligands, the holodirected structures in which the ligand atoms are connected to each other are clearly ionic, but the ionic character of the bonds decreases as the atomic number of the halogen ligand increases and greater transfer of electron density from the ligands to the lead occurs as the electronegativity of the ligand decreases and the bond become covalent bond. If the arrangement is holodirected geometry, the PbII-ligand bonds are all similar.

d) Lone pairs: Ideally the B-site displays $6s^2$ lone pair. When considering every one of these elements, of each of the 120+ elements just lead has this alluring mix of properties.

3. Coordination Engineering of Halide Perovskite Crystals

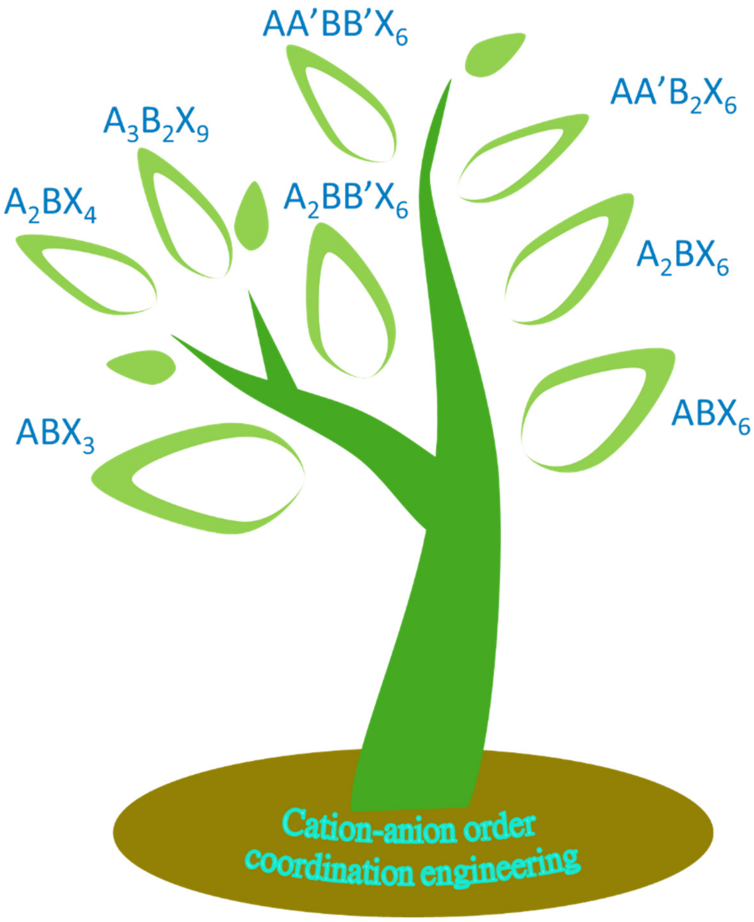
It is clear that energy materials having superior characteristics encompass the prospective to stimulate upcoming technological development. Hence, finding other new perovskites becomes important in order to overcome two vital challenges: stability and toxicity. This section provides important concepts of coordination engineering framework for engineering new perovskite materials with a special aim to improve stability and avoiding toxicity as well as provide an insight for the future directions and new research horizons of this field. To improve device efficiency crystallization process is vital. During crystallization there are two key factors that have to be considered: phase distribution and crystal orientation. Thus, phase control mechanisms are required to develop high quality crystals required for high performance device. Such phases are synthesized in the form of colloidal phase to obtain proper phase distribution and crystal orientation as shown in Scheme 2a-d. Moreover, size distribution, absorption spectra and phase transformation are quite different in different solvents such as dimethylacetamide (DMAc), DMAc: dimethylsulfoxide (DMSO), DMAc: toluene (TOL), and dimethylacetamide: toluene (HI). To understand this variation of size distribution and absorption spectra, applying coordination engineering is useful. As shown from Scheme 2, poorly coordinating solvents give proper size distribution and crystal orientation. Such properties are important for high device efficiency. This property is obtained by producing colloidal precursor solution, which is a useful procedure of producing quality crystals required for proper size distribution and crystal orientation. This situation is useful to achieve proper charge transport and thermodynamically stable solution.[17] Thus, coordination engineering is useful to obtain colloidal phase with high crystal orientaion.



Scheme 2. Phase Control via coordination engineering of Colloidal halide perovskite. Reproduced with permission.[17] Copy right, 2020, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. a) Precursor solutions for Size distribution. b) Absorption spectra in various solvents: DMAc, DMAc:DMSO, DMAc:TOL, and DMAc:TOL (HI), respectively. c) Absorption spectra of (TEA)2(MA)n−1PbnI3n-1 (n=1, 2, 3) in DMAc:TOL (HI). d) Phase transformation into random and oriented crystal orientaion.

3.1. Cation and Anion Order Engineering of New Halide Perovskite

Other than the previously mentioned structural flexibility, these halide perovskite materials have generous compositional flexibility, which is done by means of ion order engineering. Subsequently, from the viewpoint of particle arrange designing, concoction substitutions happen onto every one of the three locales of the aristotype structure. Following this, the anion site can house higher amount of vacancies and molecules exchange (e.g. halides) together while cation exchanges go up against either arbitrary or ordered orientations as appeared in Scheme 3, which affect the attributes of the designed materials.



Scheme 3. Coordination engineering of halide perovskites.

In the giant mass of $A_2BB'X_6$ perovskites the B and B' cations go up against an organized model that resembles cation and anion positions in the crystal salt structure (Figure 1). In excess of 400 revealed points of reference of shake salt can be found in $A_2BB'X_6$ perovskites.[90,91] As a general rule when the oxidation states of B and B′ differ by less than two a disordered arrangement is observed (e.g. La_2CrFeO_6),[92,93] while, a variation larger than two almost always constructs an ordered arrangement (e.g. Sr_2NiWO_6).[94] When the variation in oxidation states is just two, disordered (e.g. Sr_2FeRuO_6),[94] partially ordered (e.g. Sr_2AlTaO_6), or fully ordered (e.g. Sr_2YNbO_6) arrangements can consequence, depending on differences in size and/or bonding preference of the B and B′ cations.[95–97] There have been various broad reports of B-site cation arrange in perovskites, and the forces that drive B-site cation ordering are normally understood and reported elsewhere[91,95,98].

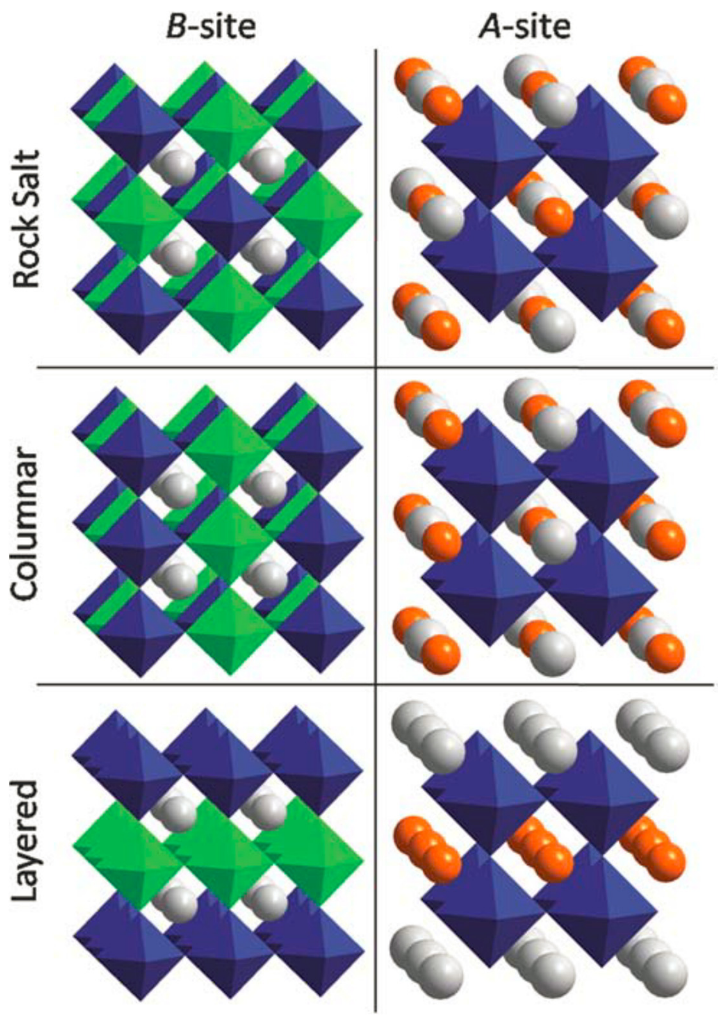


Figure 1. Perovskites structural Cation order. Reproduced with permission.[99] Copyright 2010, Royal Society of Chemistry.

3.2. ABX_3 Perovskite

The stability issues in halide perovskite materials become a default challenge for practicing. Thus, looking for other analogous materials with similar octahedral arrangement (i.e. 3D arrangement of corner-sharing octahedral BX_6 units)[100–102] or other materials that might fulfill the vision of perovskite community (i.e. edge sharing octahedral arrangement) is a must. In this section, a representative cubic crystal structure was taken on by ABX_3 perovskite halides[103] as shown in Figure 2A, where A and B are twelve- and six-fold organized, and have plus one, plus two supposed charge states, correspondingly, whereas X[104I] is a halide. On the other hand, edge sharing non-perovskite structures with a real so universal in arrangements with ABX_3 stoichiometry (for example $CsNiF_3$ and $CsCoCl_3$ crystal structures)[105]. Furthermore, from the obtainable data on formability of ABX_3 structures, the possibility to create a model and forecast by means of an acceptable correctness whether a suggested structure by means of known option of cations with +1, +2 and halide with -1 charge ought to be halide perovskite or a non-perovskite as shown in Figure 2B.

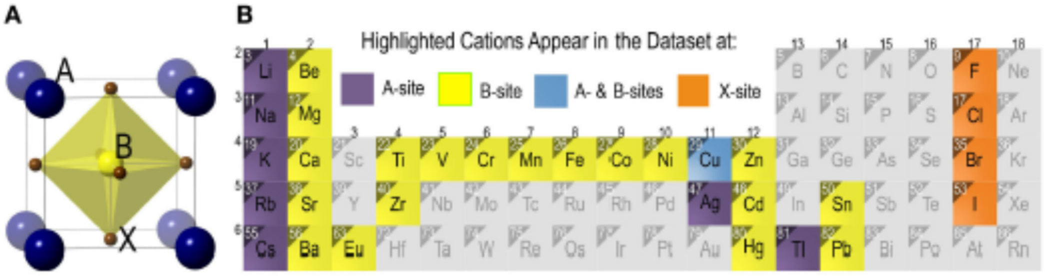


Figure 2. The ideal cubic halide perovskite with a framework of ABX_3 and its Chemical space in the periodic table. Reproduced with permission.[106] Copyright 2016, Frontiers in Materials.

3.3. *ABX_6 Perovskite*

The breakthrough with a novel ABX_6 crystal showing superior performance leads to a broad occasion for lucid representation for sophisticated optoelectronic and solar cell function.[107] Whereas the photovoltaic characteristics of Sb(III) iodides well explored previously, halide complexes of Sb(V) continue uncultivated. Furthermore, these halide complexes of Sb(V) materials are characterized hued substances[108,109] and, subsequently, can be viewed as conceivably accommodating materials for photovoltaic cells. Substance arrangement and precious crystal structure of the items emphatically rely upon the idea of organic cations A, while no unmistakable relationships empowering objective material plan have been built up so far.[110–112]

3.4. *A_2BX_4 Perovskite*

A_2BX_4 halide perovskites are two dimensional materials with BX_6 octahedra,[113] prompting adaptable mechanical properties and valuable light emission.[114,115] Furthermore, these halide perovskites can be differed by consolidating either divalent metal or an extended organic cation chain suggestive of numerous other imaginative bearings that could strengthening enhance the usefulness of these materials.

3.5. *A_2BX_6 Perovskite*

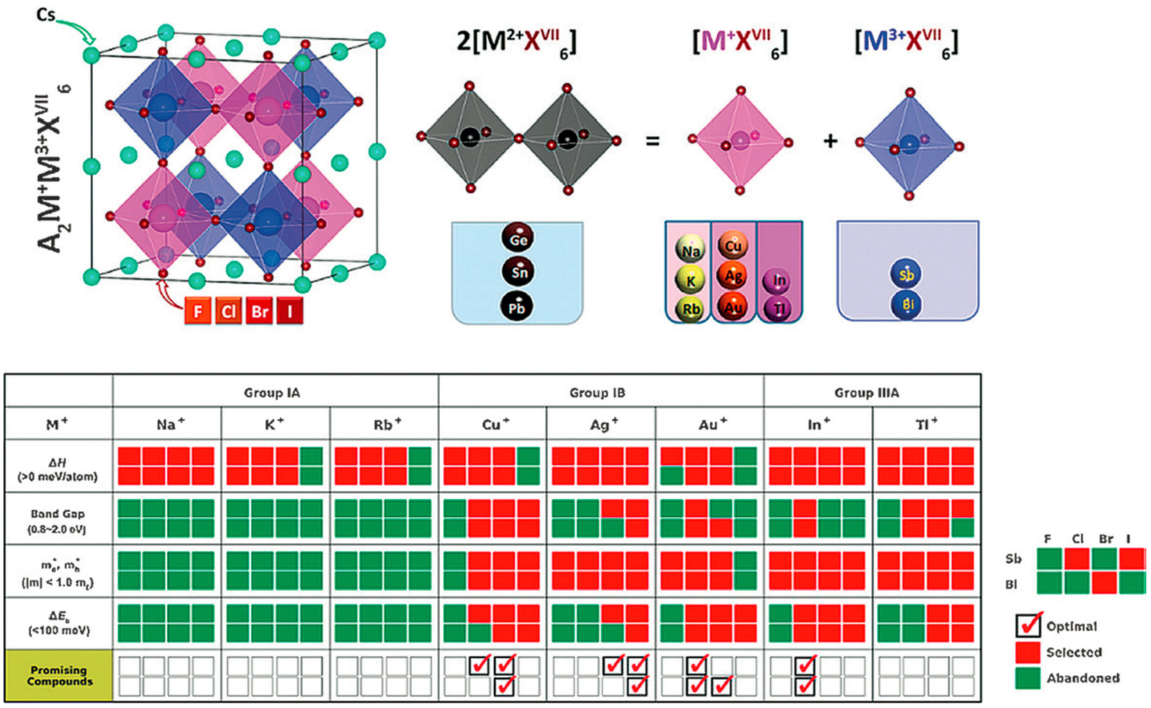
A_2BX_6 framework is another material that is expected to play its contribution. For instance, in recent times Cs_2SnI_6 is introduced; its exceptional electronic and optical properties create it a capable applicant with novel efficiency.[116] Furthermore, this outline technique has likewise propelled the comprehension of the basic security for the perovskite sunlight based device, since two dimensional $[PEA]_2[MA]_2Pb_3I_{10}$ has demonstrated superior protection from moisture[117] conceivably because of the hydrophobicity of the benzene ring.

3.6. *$A_3B_2X_9$ Perovskite-Like 3D Framework*

The majority of the new attempts have been spotlighted on the examination of halide complexes of the post transition group 15 elements for example Bi and Sb. Alongside the spearheading writes about BiI[118] and $A_3Bi_2I_9$ (A = MA or Cs),[119–122] The scope of antimony (III) halides explored in photovoltaic cells is constrained to $A_3Sb_2I_9$.[123–125] Furthermore, both $Cs_3Bi_2I_9$ and $MA_3Bi_2I_9$ are showing a different advantage over Pb- or Sn-based perovskites.[126,127] This is on the ground that the upsides of non-danger, encompassing stability, and low-temperature arrangement processability, which gives a promising answer for location the poisonous quality and stability issues.

3.7. *$A_2BB'X_6$ Double Perovskites*

The journey for a totally without Pb yet continues a noteworthy objective in the halide perovskite photovoltaic. So as to understand the 3D perovskite design this has shown favorable circumstances for high efficiency, twofold perovskite with 3D structure gets incredible consideration this time. As of late, Zhao et al.[128] found, through first-standards counts, a prosperous set of quaternary halide perovskites through $A_2B^{+}B^{3+}X_6$ in the course of the transformation of Pb^{2+} particles into one monovalent particle (B^{+}) and one trivalent particle (B^{3+}), as appeared in Figure 3. The new perovskite viably kept away from harmful Pb^{2+} cations. Additionally, all these have inborn thermodynamic solidness, appropriate band holes, little bearer compelling masses, and low excitation restricting energies. This suggests us a potential strategy for taking out harmful Pb in PSCs. It might likewise be important to dope different molecules into the $CH_3NH_3PbI_3$ cross section, or to change to different materials, for example, $Cs_2InSbCl_6$, $Cs_2InBiCl_6$, $Cs_2BiAgCl_6$, and $Cs_2AgBiBr_6$, to enhance the conventional $CH_3NH_3PbI_3$.[128–132] However, it stays testing to lead point by point examinations on the systems of perovskite light assimilation through first principal computations.



	Group IA			Group IB			Group IIIA	
M^{+}	Na^{+}	K^{+}	Rb^{+}	Cu^{+}	Ag^{+}	Au^{+}	In^{+}	Tl^{+}
ΔH (>0 meV/atom)	🟥🟥🟥🟥 🟥🟥🟥🟥	🟥🟥🟥🟩 🟥🟥🟥🟩	🟥🟥🟥🟩 🟥🟥🟥🟩	🟥🟥🟥🟩 🟥🟥🟥🟩	🟥🟥🟥🟥 🟥🟥🟥🟥	🟥🟥🟥🟩 🟩🟥🟥🟩	🟥🟥🟥🟥 🟥🟥🟥🟥	🟥🟥🟥🟥 🟥🟥🟥🟥
Band Gap (0.8~2.0 eV)	🟩🟩🟩🟩 🟩🟩🟩🟩	🟩🟩🟩🟩 🟩🟩🟩🟩	🟩🟩🟩🟩 🟩🟩🟩🟩	🟩🟥🟥🟥 🟩🟥🟥🟥	🟩🟩🟥🟥 🟩🟩🟩🟥	🟩🟥🟩🟩 🟩🟥🟥🟩	🟩🟥🟩🟩 🟩🟥🟩🟩	🟩🟥🟥🟥 🟩🟥🟥🟩
m_e^*, m_h^* (|m| < 1.0 m_0)	🟩🟩🟩🟩 🟩🟩🟩🟩	🟩🟩🟩🟩 🟩🟩🟩🟩	🟩🟩🟩🟩 🟩🟩🟩🟩	🟩🟥🟥🟥 🟩🟥🟥🟥	🟥🟥🟥🟥 🟥🟥🟥🟥	🟥🟥🟥🟩 🟥🟥🟥🟩	🟥🟥🟥🟥 🟥🟥🟥🟥	🟥🟥🟥🟥 🟥🟥🟥🟥
ΔE_b (<100 meV)	🟩🟩🟩🟩 🟩🟩🟩🟩	🟩🟩🟩🟩 🟩🟩🟩🟩	🟩🟩🟩🟩 🟩🟩🟩🟩	🟩🟥🟥🟥 🟩🟩🟥🟥	🟩🟩🟥🟥 🟩🟩🟩🟥	🟩🟥🟥🟥 🟩🟥🟥🟥	🟩🟥🟥🟥 🟩🟥🟥🟥	🟩🟩🟥🟥 🟩🟩🟥🟥
Promising Compounds	☐☐☐☐ ☐☐☐☐	☐☐☐☐ ☐☐☐☐	☐☐☐☐ ☐☐☐☐	☐☑☑☐ ☐☐☑☐	☐☐☑☑ ☐☐☐☑	☐☑☐☐ ☐☑☑☐	☐☑☐☐ ☐☑☐☐	☐☐☐☐ ☐☐☐☐

	F	Cl	Br	I
Sb	🟩	🟥	🟩	🟥
Bi	🟩	🟩	🟥	🟩

☑ Optimal
🟥 Selected
🟩 Abandoned

Figure 3. First-principle demonstrations of cation-variation to propose stable lead-free halide perovskites for photovoltaic applications. Reproduced with permission.[128] Copy right 2017, American Chemical Society.

3.8. *AA′B_2X_6 Double Perovskite*

Gulzhanat *et.al.* performed ab-initio calculations of $CsRbPb_2I_6$ halide perovskites with ferroelectric AA′B_2X_6 perovskite framework.[133] The watched unconstrained polarization of AA′B_2X_6 perovskite materials is relied upon to be one of the critical properties which decide efficiency of perovskite based sunlight based cells. The unit cell of perovskite contains 20 atoms. Space group of [001] layered supercell is Pmc21, [111] rocksalt supercells space assemble is Pna21, this is really a polar space bunches appeared in Figure 4.

doi:10.20944/preprints202403.1615.v2

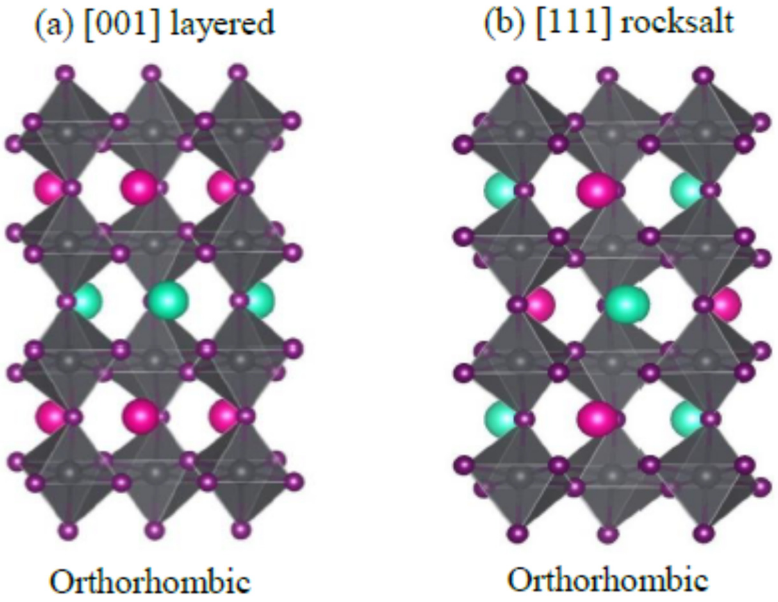
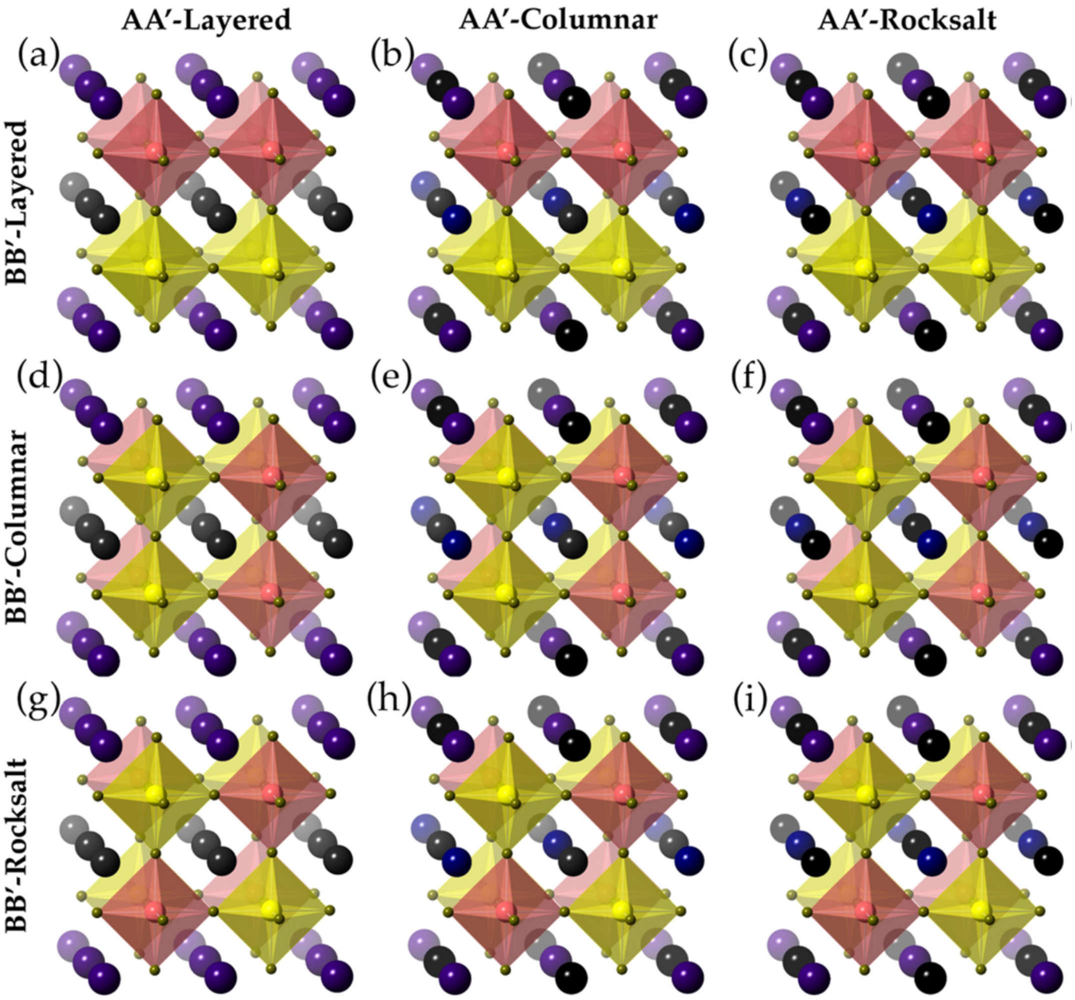


Figure 4. Structure of $CsRbPb_2I_6$ superlattices in [001] and [111] directions. Reproduced with permission.[134] Copy right 2015, ANM abstracts.

3.9. AA'BB'X₆ Double Perovskite

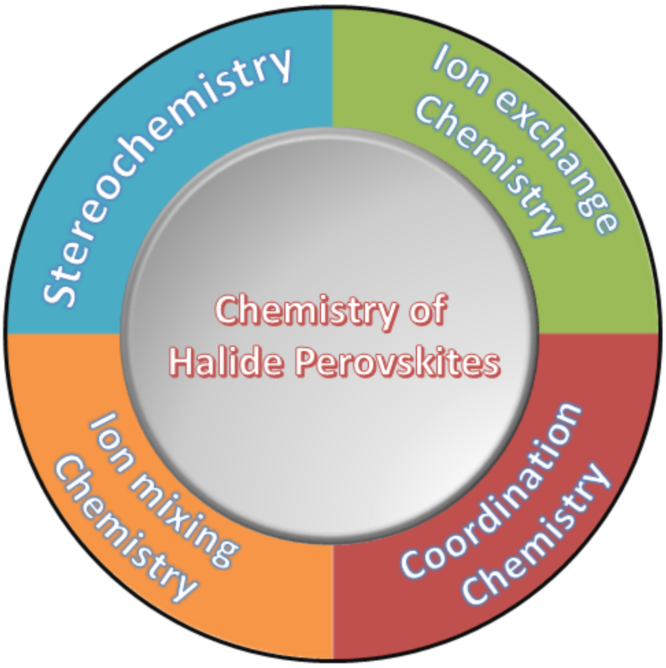
Within twofold $AA'BB'X_6$ crystal structures through one:one proportion of its components, layered, columnar, and rocksalt become unique potential outcomes for requesting on every one of the A- and the B-site cation sub-cross sections. On account of columnar requesting cations of a similar kind are ceaseless just along one measurement and shape sections of interfacing Cl octahedra, while for the instance of layered requesting cations of every sort frame on the other hand stacked 2D planes. At last, the rocksalt requesting, which speaks to the the majority of symmetric one out of the three conceivable outcomes, known as in light of the fact that the example of A-site or B-site is comparable to the anion and cation arrangement observed from rocksalt structures. For this situation, cations substitute in every one of the three symmetrical headings. The halfway replaced cations at A- and B-destinations result an aggregate of 9 unique potential outcomes for $CsRbCaZnCl_6$ (Scheme 4).



Scheme 4. The 9 promising cation ordered patterns investigated in the one: one ratio of its elements of double perovskites. Reproduced with permission.[135] Copy right 2015, Applied Physics.

4. Coordination Chemistry of Halide Perovskite Structures

The investigation of lead halide structures (Scheme 5) is well established.[136] Furthermore, change metals with an s^2 electron setup (e.g., Ti^{4+}, Sn^{2+}, Pb^{2+}, Sb^{3+}) speedily encounter complexation with halide particles. Lead buildings are typically implied as "plumbates" (e.g., triiodoplumbate (PbI_3^-)) and fill in as forerunners in arrangement. Right when separated in DMSO, PbI_2 is dreary yet winds up darker unending supply of plenitude iodide particles. As planning dissolvable ligands are superseded by I^- course of action of PbI_3^- and PbI_4^{2-} buildings, cutting down imperativeness charge-trade retention groups is observed.[136] These new advances can be quickly pursued and give understanding into complexation events in the forerunner arrangement.



Scheme 5. Important chemistry concepts that should be considered during coordination engineering of halide perovskites.

Figure 5 indicates retention spectra of PbI$_2$ recorded at various I$^-$ focuses in DMF. The reliance of ingestion on the I$^-$ fixation empowers estimation of complexation constants, as appeared in Equation 1 and 2, respectively.[137]

$$PbI_2 + I^- \leftrightarrow PbI_3^- \ \left(K_1\right) \tag{1}$$

$$PbI_3{}^- + I^- \leftrightarrow PbI_4{}^{2-} \left(K_2\right) \tag{2}$$

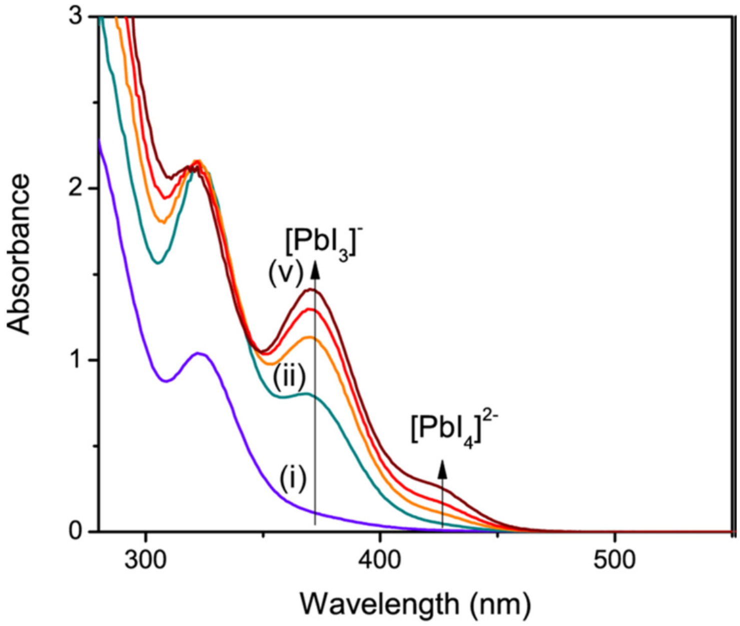
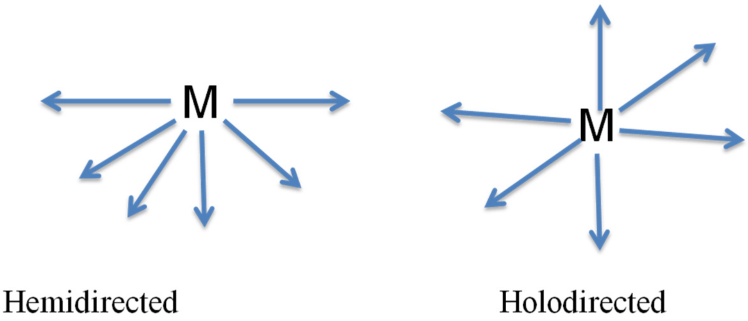


Figure 5. Absorption spectra of PbI$_2$ in DMF with rising amount of CH$_3$NH$_3$I. Reproduced with permission.[136] Copy right 2015, Royal Society of Chemistry.

It is spellbinding to see that the complexation of Pb (II) with iodide particles is free of the likelihood of the iodide counter molecule. Close spooky highlights relating to lead halide structures were in like way observed when CH_3NH_3I was supplanted with KI. An issue by and large examined in considering the coordination and stereochemistry of liberal metals is that of the 'stereochemical movement' of valence shell lone electron sets.[138–142]

4.1. Coordination Chemistry of Post Transition Metal Atoms

Of all p-block elements, lead(II) has a specific interest for coordination chemists,[143] as it can receive a wide range of geometries in its complexes, permitting a degree of tolerance for ligand arrangements which isn't seen in, for instance, d-block components. The capacity to tie well to both hard and delicate benefactor iotas make lead (II) an intriguing metal to think about. Lead(II) structures have also pulled in incredible intrigue in light of lead's huge particle span, changeable coordination number, and the conceivable event of a stereochemically dynamic solitary combine of $6s^2$ external electrons and in addition novel system topologies.[144] Consistent with the hard-delicate corrosive base hypothesis, the moderate coordination capacity of Pb (II) implies that it can adaptably facilitate little nitrogen or oxygen iotas and additionally huge sulfur atoms.[145] The examination of "stereo-synthetic action" of valence shell electron solitary matches in polymeric and supramolecular mixes might be additionally intriguing.[146] Lead (II) has an electronic structure $[Xe]4f^{14}5d^{10}6s^2$. Because of relativistic impacts the 6s orbital is contracted and settled. This settled 6s sets lessens its cooperation in the science of the component (turning into an “inert-pair”) and this clarifies why inorganic Pb frames mixes in a lower oxidation state (less by two) than would be normal from its gathering number.[147] The evident hesitance of the 6s electrons to assume a role in the science of the component may likewise influence the stereochemistry of Pb (II) edifices. This impact can be comprehended as far as basic hybridization or valence shell electron-match shock arguments. [148] It appears that the 6s orbital, despite its adjustment, can hybridize with the 6p orbitals to give a "stereochemically dynamic" 6s electron combine possessing one position in the coordination circle of the metal. Since the match is not specifically discernible, its quality is typically recognized by a void in the conveyance of the coordination bonds (asymmetrical coordination (hemidirected), as see in Scheme 6). On the off chance that hybridization does not happen and the combine has just s character, at that point it is "stereochemically latent" and the complex does not demonstrate a hole or void in the security appropriation (symmetrical coordination (holodirected) in Scheme 6).[149]



Scheme 6. Hemidirected and holodirected coordination sphere of lead(II). Reproduced with permission.[149] Copy right 1998, American Chemical Society.

4.2. Proposed Ion Exchange and Ion Mixing Chemistry in Perovskites

Figure 6 shows the various types of ion exchange, substitutions and ion mixing attempted for engineering new perovskite families. The figure provides a simple basis for a discussion and is an indicative of many perovskite structures for many optoelectronic applications. If the proposed cation and anion exchange and substitution become successful, there will be a chance of improving the stability and overcoming the toxicity: the two most challenging issues for future commercialization of halide perovskites. These exchanges and substitutions and mixing of ions take place at the A site, B site and X site and the ion mixing can take place in all sites.

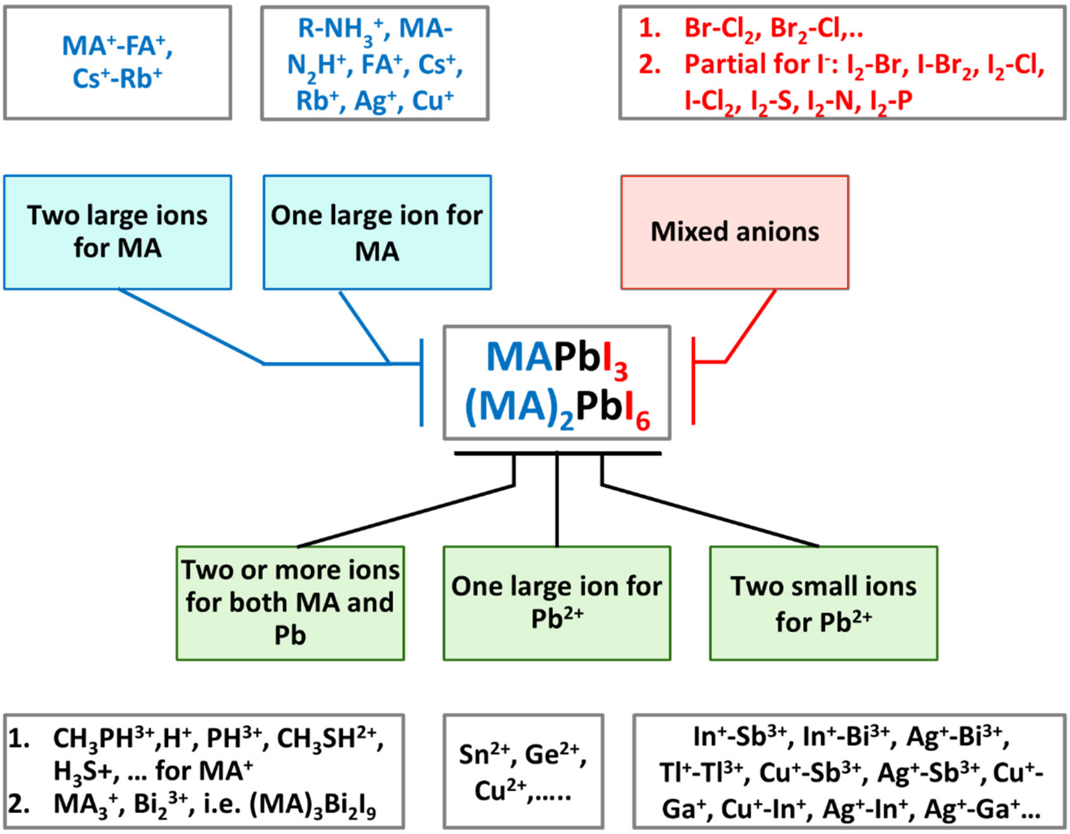


Figure 6. Chart illustrating types of multiple ion substitution in the organic-inorganic halide perovskite lattice.

Figure 7 shows the total viewpoint of the strategy used for a halide substitute method of cesium lead halide quantum specks. Halide substitute is useful for getting the cubic $CsPbI_3$ which was normally gained at higher temperatures. Hoffman et al.[150] used a $CsPbBr_3$ quantum dots film and transformed it to a cubic $CsPbI_3$ arrange by diving the $CsPbBr_3$ quantum dots layer (~75-nm thickness) into the iodide forerunner. In this way, the technique for halide trade process in cesium lead halide quantum specks is greatly direct and this strategy can swear off using the surface functionalization.[151]

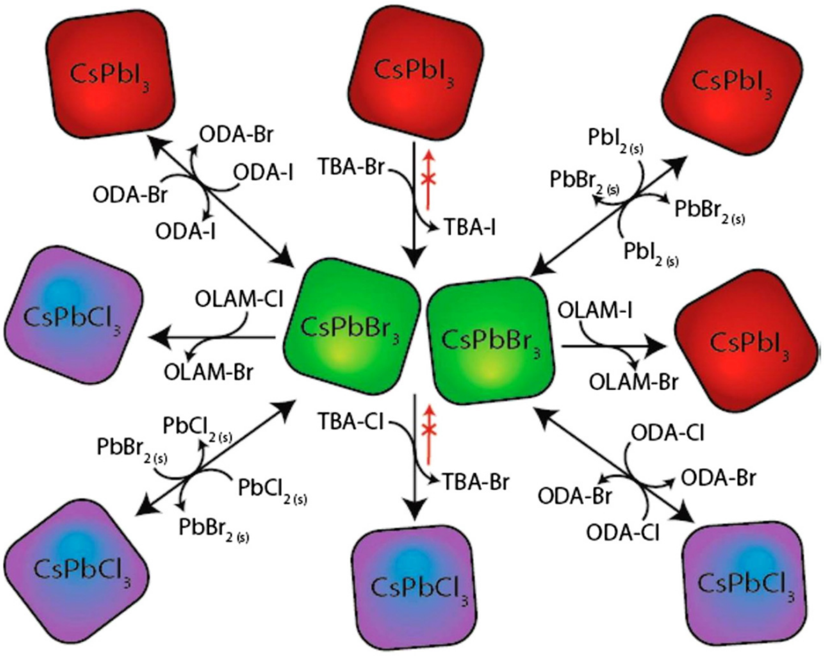


Figure 7. The combined procedure of a characteristic anion exchange process and precursors on $CsPbX_3$ (X = Cl, Br, I) quantum dots. Reproduced with permission.[152] Copy right 2015, American Chemical Society.

4.3. Coordination Chemistry of Single Crystal Complexes Formation

Grasping crystal development system is extraordinarily significance for headway and manufactured strategies for additional functions. Typically, valuable precious crystal development in solution can be segregated via three central forms: in situ change and dissolution−crystallization.[153] Furthermore, It has been established that the vitality of such valuable precious processes of crystal advancement decidedly relied upon the CH_3NH_3I concentration.[154] Then, lead iodide completely organized with iodine particles in order to frame in an iodine prosperous condition (Equation 3):[155]

$$\mathrm{PbI_2 + xI^- \rightleftharpoons PbI_{2+x}^{x-}},\ (x=1,2) \tag{3}$$

At that point lead complex additionally went about as building units to recrystallize into a thermodynamically supported morphology within the sight of ammonium cations (Equation 4).

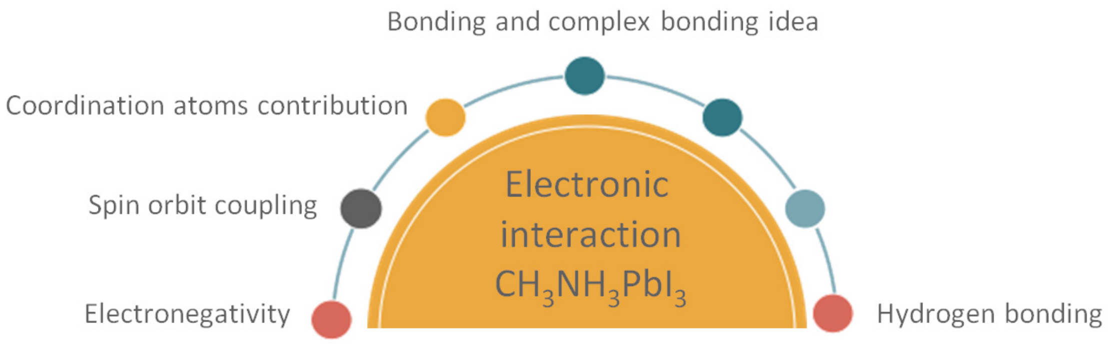
$$\mathrm{CH_3NH_3^+ + PbI_{2+x}^{x-} \rightleftharpoons CH_3NH_3PbI_3 + (x\text{-}1)I^-},\qquad (x=1,2) \tag{4}$$

4.4. Coordination Chemistry Limits Crystallization of Halide Perovskites

Photovoltaic perovskites field is slowly shifting from highly disordered[156] perovskite solar cells towards generation of single crystal[157] devices which can ultimately provide lower energy losses. Competition between iodides with solvent molecules to coordinate lead atoms will determine the species present during perovskite nucleation and growth. Low complexity DFT calculations help to understand solvent coordination ability and can be used as a tool to screen suitable solvents. Highly coordinating solvents such as DMSO will form partially covalent bonds with lead retarding crystallization kinetics and its subsequent removal may be difficult. Poorly coordinating solvents like GBL will not be able to stabilize PbI_3^- moieties enabling a fast reaction with the methyl ammonium cation. Importantly, water present in environmental humidity can be regarded as an additive which retards perovskite crystallization.

5. Electronic Interaction during Coordination Chemistry

In this section we have discussed about bonding and complex bonding ideas, hydrogen bonding, electronegativity, electron localization, cation-anion orbital interaction and spin orbit coupling on the electronic structure as shown in Scheme 7. All these essential concepts are the results of electronic interactions and provide important electronic characteristics for much electronic functionality as discussed in next section 5.



Scheme 7. Possible electronic interaction mechanism in constructing the electronic structure of $CH_3NH_3PbI_3$.

5.1. Bonding Idea in Lead Halide Perovskites

The lead halide perovskites are direct bandgap materials. Despite the fact that this direct bandgap nature is a substantial speculation, there are ongoing computations recommending special cases that happen in noncentrosymmetric halide perovskite on account of splitting.[158–163] Furthermore, electronic structure close to the band edge is primarily expressed as the fundamental BX_6 units.[164–169] Consequently, orbital outlines of segregated $[BX_6]^{4-}$ bunches, similar to those in the zero dimension $(CH_3NH_3)_4[PbI_6]\bullet 2H_2O$[170] give a base for thoughtful more multifaceted band structures. For $[PbI_6]^{4-}$ units specifically, a Pb 6s–I 5p σ-antibonding orbital contains the most noteworthy involved sub-atomic orbital (HOMO), while Pb 6p–I 5p π-antibonding and Pb 6p–I 5s σ-antibonding orbitals include the least abandoned sub-atomic orbital (LUMO) (Figure 8A).[166]

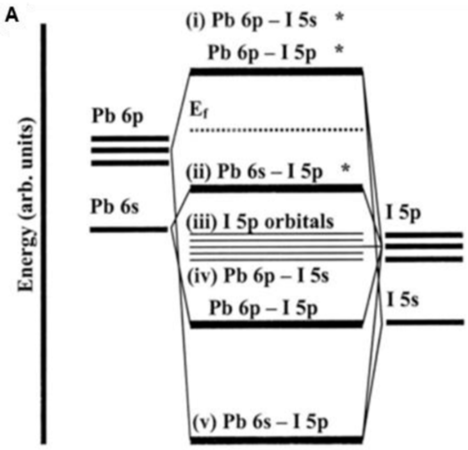


Figure 8. (A) Bonding illustration of isolated $[PbI_6]^{4-}$ complex ion exclusive of allowing for spine orbit coupling. Reproduced with permission.[171] Copy right 2003, American Physical Society. (B) Band structure of $CH_3NH_3PbI_3$. Reproduced with permission.[172] Copy right 2014, American physical Society.

The chemical bonds of the ions directly impact the perovskite structure; however, it can be challenging to directly link experimental results to theoretical calculations. Consequently, Brown[173] developed *bond valence theory* as a way of linking empirical bond lengths to theoretical bond valences. Bond valence theory also apparently predicts both bond length and stability (Equation 5). The number resulting from Equation 4 is the total bond valence sum of that ion:

$$BV = \sum_{N} \exp\left[\frac{R_0 - R_{A\text{-}X\ or\ B\text{-}X}}{b}\right] \tag{5}$$

where BV is the valence of the A-X or B-X bond, R_0 and b are empirically determined parameters, and R(A-X or B-X) is the experimentally determined A-X or B-X bond length.

In 2001, Lufaso and Woodward [174]used the bond-valence method to back-calculate ionic radii to calculate a so-called bond-valence tolerance factor. The bond valence tolerance factor (t_{BV}) may be a powerful method for predicting perovskite stability, but foreknowledge of the bond valence parameters is needed. It also fails to account for stoichiometric structural vacancies. In 2009, Ubic[175] derived a tolerance factor model as a function of the cubic/pseudocubic lattice constant, r_B and r_X (Equation 8), which accounts for A-site point defects.

$$t_{BV} = \frac{R_{0(A-X)} - B\ln\left(V_A / N_A\right)}{\sqrt{2}R_{0(B-X)} - B\ln\left(V_B / N_B\right)} \tag{6}$$

where $R_{0(A\text{-}X)}$ and $R_{0(B\text{-}X)}$ are the unit valence bond lengths of the A-X and B-X bonds, V_A and V_B are the ideal valence states of the A and B cations, N_A and N_B are their coordination, and B = 0.37. The ratios V_A/N_A and V_B/N_B are bond strengths for A-X and B-X, respectively.[176]

$$t_1 = \frac{a_c - 0.05444}{0.66046\left(r_B + r_X\right)} - 1.981012 \tag{7}$$

Where, $a_c = 0.05444 + 0.46701\left(r_A + r_X\right) + 1.30838\left(r_B + r_X\right)$ and is cubic lattice constant

The a_{pc} (average relative error = 0.60%) is given by equation 8:

$$a_{pc} = 0.06741 + 0.4905\left(r^{VI}_{A(id)} + r^{VI}_{X(id)}\right) + 1.29212\left(r_B + r^{VI}_{x}\right) \tag{8}$$

Where, $\mathrm{r}^{\mathrm{VI}}_{\mathrm{A(id)}}$, r_{B} and $\mathrm{r}^{\mathrm{VI}}_{\mathrm{X(id)}}$ effective ionic radii of A, B nd are X ions in six fold coordination. For the pseudocubic lattice, t_1 can be calculated as in equation 9

$$t_1 = \frac{a_{pc} - 0.011730139}{0.07209203\left(r_B + r_X\left(id\right)\right)} - 1.760998 \tag{9}$$

Therefore, these bonding parameters are helpful to understand how the bonding interaction, electronic interaction and coordination chemistry takes place which give information on the distortion and tolerance factor of the structure formed. It also provides information on what bonding parameters are important during electronic interactions. It is primarily important in validating chemical structures.

5.2. Complex Bonding Idea in Lead Halide Perovskites

The leading complex bonding between the A site cation and BX_3^- complex anion is electrostatic. Furthermore, there is a strong electrostatic potential (~8 V) holding the cation at its lattice site. For instance, the positively charged ion, $CH_3NH_3^+$, is within a negatively charged cage, PbI_3^-. Moreover, further electrostatic role to the chemical bonding between the molecular dipole and the PbI_6 octahedra is the charge–dipole interaction, which depends on the dipole orientation. Similarly, there is also the consequence of prime polarization. An induced dipole interaction is expected owing to the substantial polarizability of the iodide ions (ca. 7×10^{-24} cm^3). Because of these interactions, a molecular orientation correlation with octahedral deformation in molecular dynamic simulations is strongly expected[177] and more comprehensive investigations are continuing. Additionally, the van der Waals interactive forces together explain the intermolecular and Debye force interactions.

5.3. Electronegativity and Electronic Bandgap Tuning

From the perspective of band structure, bandgap tuning and structure factor, it is highly recommended to consider all electronic interactions such as electronegativity of each atom making the semiconductor materials. For instance, the band gap for $CH_3NH_3SnI_3$ ranges from 1.2–1.4 eV, while the 1.5–1.6 eV band gap values for $CH_3NH_3PbI_3$.[178,179] Thus, Pb (1.87) has a smaller Pauling electronegativity contrasted to Sn (1.96),[179] indicating the band structure of Pb states have to be higher and thus larger bandgap values. Hence, Sn is less metallic in contrast to Pb and therefore, Sn–I interactions have to be less ionic in contrast to Pb–I interactions, suggesting smaller band gap belongs to $CH_3NH_3SnI_3$. As confirmed from the conduction band edges of $CH_3NH_3SnI_3$ and $CH_3NH_3PbI_3$ at −4.17 eV and −3.90eV, correspondingly, i.e. Pb states are positioned higher in the band structure of $CH_3NH_3PbI_3$.[180] Hence, considering the influence of electronegativity on the band structure is vital.

5.4. Cation-Anion Orbital Interaction

A cooperation between any two orbitals ϕ_i and ϕ_j, be it degenerate or nondegenerate, prompts two new vitality levels that look as though the collaboration repulses the associating levels from one another. As needs be, the orbital connection of an anion with a cation is naturally balancing out, on the grounds that it includes the cooperation of an unfilled level ϕ_i of a cation with a filled level ϕ_j (often, a solitary combine orbital) of an anion (Figure 10).

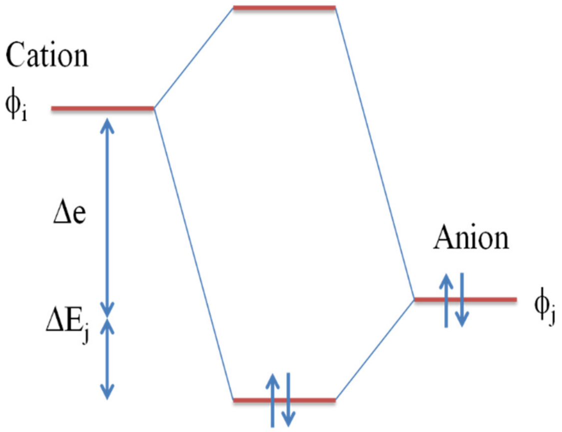


Figure 10. Representation of energy stabilization via the interaction of filled anion orbital and empty cation orbital.

This vitality adjustment is corresponding to the square of the cover indispensable $S_{ij} = \langle\phi_i|\phi_j\rangle$ and is contrarily relative to the vitality distinction $\Delta e_{ij} = |e_i - e_j|$ between the two orbitals, $S_{ij}^2/\Delta e_{ij}$.[181] When a cation is encased in an enclosure of anions (e.g., the A cation of ABO_3 in a B_8 block and proportionately in a confine of $12O^{2-}$ anions), the aggregate adjustment vitality ΔE_{tot} related with the cation-anion cooperation is gotten by summing up every individual commitment as in Equation 10,

$$\Delta E_{tot} = \sum_j \Delta E_j \alpha - \sum_j \frac{S_{ij}^2}{\Delta e_{ij}} \tag{10}$$

The extent of the cover vital S_{ij} diminishes exponentially as the interatomic remove r_{ij} increments. This prompts some stretched and contracted cation-anion bonds inside the enclosure. The cation-anion orbital interaction is an essential way to understand bonding in halide peroveskites including crystal structure (Figure 11a), Br^- concentration dependent band gap (Figure 11b), band edges of $MAPbI_3$, $MA(Pb_{0.75}Sn_{0.25})I_3$, $MA(Pb_{0.25}Sn_{0.75})I_3$, $MASnI_3$ (Figure 11c) and Phase change from orthorhombic in to yellow phase as shown in Figure 11a-d.[182] In this case, the main interaction players are coordination engineering, coordination chemistry and electronic interactions that everyone shall understand. In depth understanding of these concepts is vital to understand material formation process and properties. Not only these parameters but also chemical species such as halide concentration, phase of the material formed, orbital interactions and the role played by each factor are important points that have to be considered.

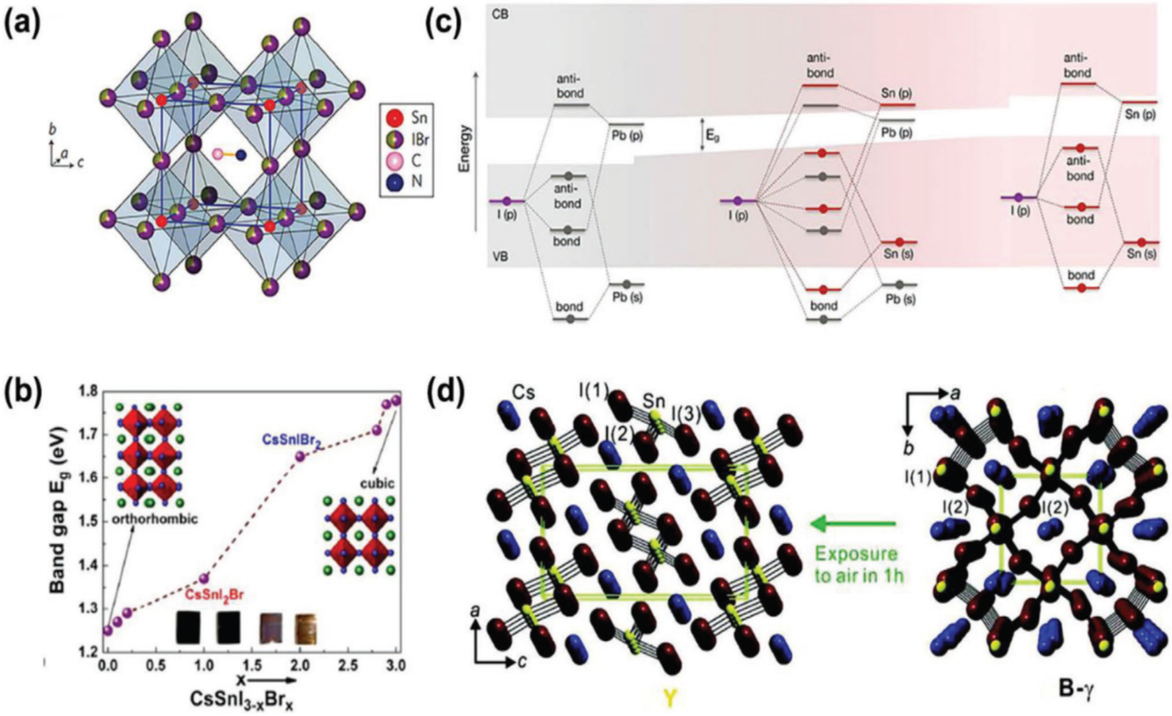
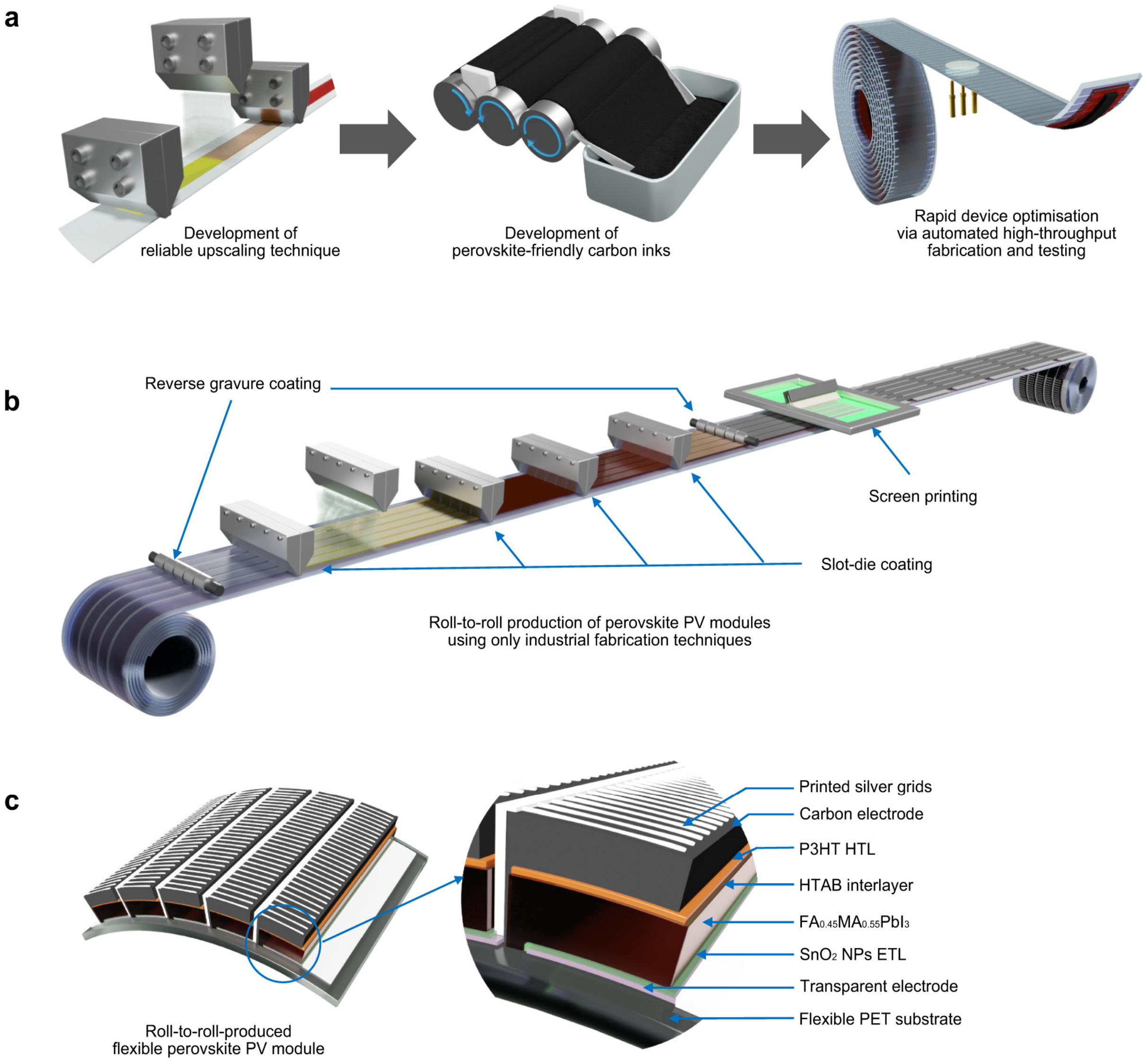


Figure 11. Cation anion orbital interaction creating bonding in halide perovskites. Reproduced with permission.[182] Copy right 2020, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

As shown in Figure 11b, the concentration of Br- ion varies the band gap. Increasing concentration of Br- ion increases the band gap. This indicates that optimum concentration of halide anions shall be validated for optimum band gap to enhance absorption capacity of the semiconducting material. On the other hand, the orbital interaction such as M-X_6 octahedral interaction determines the origin of bad gap and hence the efficiency in a given semiconductor as shown in Figure 11c. In halide perovskites such as lead and tin based perovskites the conduction band contains p orbital of the metal (M) while the valence band contains dominantly p orbital of the halide anions forming M-X, X= I^-, Br^-, Cl^-. Thus, the electronic structure of halide perovskites dependes on the oribital interactions whether to be with higher band gap or small band gap.[183–185]

6. Properties of Different Halides Perovskite Structure

What properties play a guiding role in the future development of halide perovskite materials? This question is great question with the possibility to flourish the future development of halide perovskites in various wide range applications. Halide perovskites structures have promising properties that nurture future development in various applications. Because of high dielectric constant,[186] unique ambipolar charge transport,[187,188] high quantum yield photoluminescence[189] and optoelectronic properties[190] such as high carrier mobility, long diffusion lengths, high optical absorption,[191] halide perovskites get extraordinary advantage of high efficiency,[4] low cost and compatibility with roll-to-roll fabrication technologies[192–196] including screen or ink-jet printing[197] and screen printing (Scheme 6)[198–202] from which renaissance of halide perovskites get succeed revolutionizing wide range of applications.[203,204] Moreover, the metallization of peroveskite solar cell also attract its own attention for the future development of the field.[205] Thus, the structure property relations of perovskite materials make them highly attractive for the future developments of durable perovskite solar cell and other possible applications.[206] As shown in Scheme 6a-c, roll-to-roll fabrication of tandem perovskite solar module is prepared for comercial purpose.



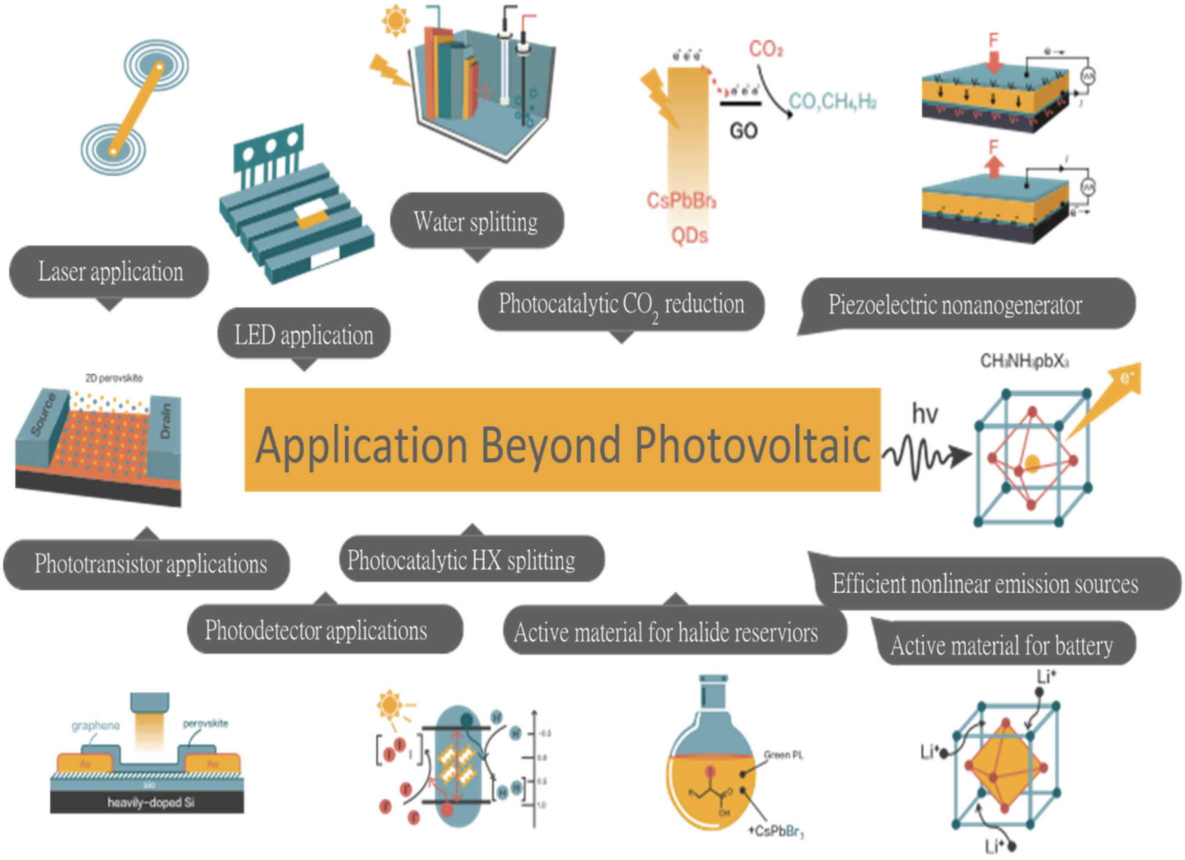
Scheme 6. Schematic diagram of screen printing for roll-to-roll production of halide perovskite. a) coting process, b) roll to roll production and c) structure of series connected module. Reproduced with permission.[192] Copy right 2024, Nature Publishing Group.

7. Energy Applications of Halide Perovskites beyond Photovoltaic

In recent times, the energy function of halide perovskite beyond photovoltaic has been lengthened with excellent results to light-emitting devices,[207] opportunity for innovative and cutting edges for perovskite based lasers,[208] light-emitting diodes (LEDs),[209] and field-effect light-emitting transistors (FETs),[210] photodetectors, nonlinear emission sources, efficient water, CO_2 and HX splitting, photocatalytic activities, active material in lithium and sodium ion batteries, halide reservoir in catalysis system and piezoelectric generators (Scheme 7), which are the main focus of this section.

7.1. $MAPbI_3$ as a Photocatalytic Material for HI Splitting

The simultaneous oxidation response engaged with HX part delivers esteem included synthetic substances, for example, I_2/I_3^-, Br_2/Br_3^-, or Cl_2, which have an assortment of employments in the vitality and cleanliness industries.[211–216] Indeed, many spearheading works show fruitful HX splitting.[214–217] By using a Nafion-isolated silicon micro-wire cathode, HI part has been accomplished with a 0.6% proficiency and unadulterated products.[218] Furthermore, Park et.al.[219] utilized $MAPbI_3$ as a photocatalytic material in unique balance with fluid HI arrangement. The vibrant harmony between the $MAPbI_3$ hastens and the soaked fluid arrangement is affirmed by means of replacement of I with Br. $MAPbI_3$ experiences a stage change to hydrated stages or PbI_2 at various particle exercises in the watery arrangement, and is steady just in particular fixation scopes of I^- and H^+. It has been discovered that the $MAPbI_3$ powder in the watery HI arrangement could adequately part HI into H_2 and I_3^- under obvious light illumination, the proficiency of which could be expanded by means of warm toughening in a polar dissolvable environment and by utilizing a Pt cocatalyst.[219]



Scheme 7. Energy applications of halide perovskite beyond photovoltaic.

7.2. Perovskite QD-GO Nanocomposite for Photocatalytic Reduction of CO_2

Reduction of CO_2 can be achieved either electrochemical or photocatalytic reduction process. The look for a superior contender has not yet rested. Current and fast growths in halide perovskite materials have activated huge attention amongst investigators for optoelectronic functions, particularly, solar cells.[220–222] Furthermore, encouraged from the accomplishments of photovoltaic, these semiconductors are main contenders for performing proficient photosynthesis if the tremendous feature instability concerns of halide perovskites can be decided primarly.[223,224] Because of its improved stability, a $CsPbBr_3$ Quantum Dot/Graphene Oxide Composite was drawing for the photocatalytic reduction of CO_2 to ethyl acetate (Figure 11).[225]

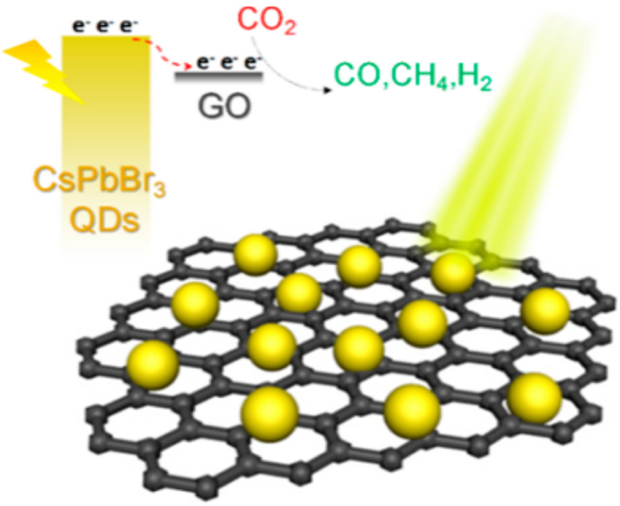


Figure 11. Representation of CO_2 photo reduction using $CsPbBr_3$ quantum dot/graphen oxide. Reproduced with permission.[225] Copy Right 2017, American Chemical Society.

7.3. Halide Perovskite as Active Material for Battery

In parallel to photovoltaic uses, halide perovskites have been proposed as their use as active material for lithium-ion battery (LIB) anodes. Hybrid organic-inorganic halide perovskites such as methylammonium lead bromide ($MAPbBr_3$) exhibits reliable values of ≈200 mA h g^{-1} with an outstanding rate potential as shown in Figure 12.[226] These preliminary results are comparable to current commercial anodes capacities. Xu *et.al.* was also demonstrated the utilization of perovskite powered charging batteries of lithium amassed with a $LiFePO_4$ cathode and a $Li_4Ti_5O_{12}$ anode.[227] This device demonstrated a high electric change and capacity effectiveness of 7.80% and superb cycling dependability, which outflanks other revealed lithium-particle batteries. The newly introduced self-chargeable power units based on integrated halide perovskite solar cells and lithium-ion batteries hold promise for various possible functions.

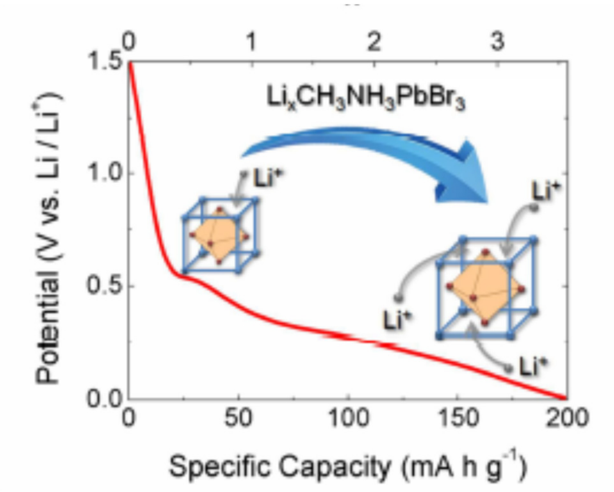


Figure 12. Intercalation of Li ion in to $CH_3NH_3PbBr_3$ and $Li_xCH_3NH_3PbBr_3$ functioning as lithium ion battery. Reproduced with permission.[226] Copy Right 2017, American Chemical Society.

Note that $CH_3NH_3PbBr_3$ accumulates then two principal preferences: (i) it considers high inclusion fixations with x>>1, and at the same time (ii) it displays little auxiliary mutilations. Critically, the rate ability does not show huge decrease for charging flows between 1 ^{0}C and 0.25 ^{0}C, demonstrating great probability for functionalities in the field of energy storage devices such as battery.

7.4. Halide Reservoir in Catalysis Applications

From the perspectives of catalysis, it is important to find a material that reserve halides. In supporting this idea, in recent times, perovskite nanoparticles (P-NPs) were prepared at the nanoscale through extraordinary size- and halide-tuned optical properties.[228,229] Of curiosity to the synthetic chemist is the apparently effortlessness where P-NPs experience composition alteration by swap using halides, as revealed at bulk[230] and at nanointerfaces.[231–233] Besides, Doane *et.al.* at that point found the capability of the P-NPs to continue as halide repositories for Finkelstein operation responses in halide perovskite, which give an uncommon colorimetric report of response kinetics.[234] Furthermore, it was hypothesized[234] that P-NPs might have the capacity to (1) fill in as a wellspring of high centralizations of halides synergist reservoir,[235] (2) screen free halide spotlight alteration of amid halide disposal reactions, [236] and (3) fill in as a quick subjective/quantitative colorimetric examine of free particles in arrangement. Figure 13 delineates these thoughts. As a halide supply (Figure 13a), the P-NP and its dynamic halide−ligand complex[237] supply halides in nonpolar environment that can respond and operated with halide perovskites, whereas in the meantime demonstrating colorimetric input. As a measure (Figure 13b), tested responses or questions ions are acquainted by means of P-NPs aliquots of recognized fixation whose shading change can give quantitative colorimetric reaction and consolidating, path a and b can give an immediate methodology toward colorimetric observing of compound responses continuously.

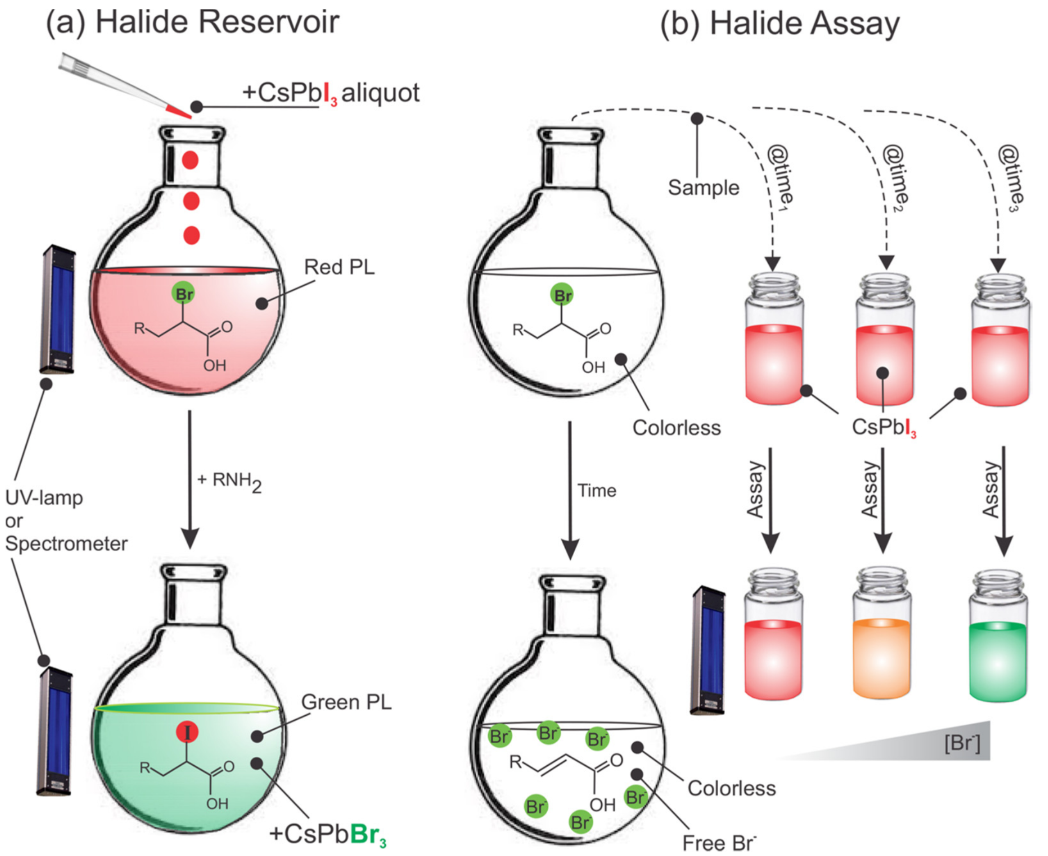


Figure 13. Graphic representation of P-NPs as halide reservoirs and colorimetric probes. Reproduced with permission.[234] Copy right 2016, American Chemical Society.

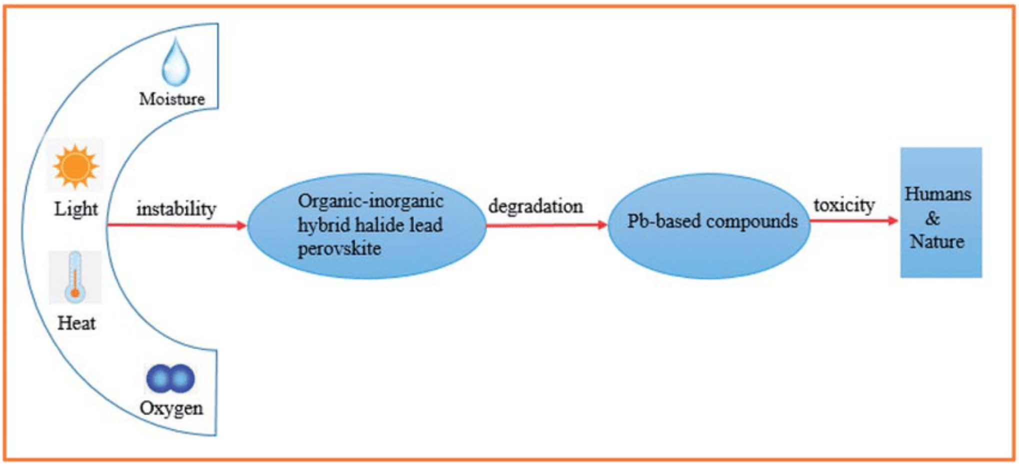
7.5. Piezoelectric Generators

It is very intriguing that a half and half piezoelectric nanogenerator in view of combinations of piezoelectric $HC(NH_2)_2PbBr_3$ nanoparticles and polydimethylsiloxane polymer has been manufactured.[238] Furthermore, the $HC(NH_2)_2PbBr_3$ nanoparticles contain all around created ferroelectric properties with high piezoelectric charge coefficient (d_{33}) of 25 pmV^{-1}.[238] The adaptable device showed elite with a greatest recordable piezoelectric yield voltage of 8.5 V and current thickness of 3.8 μAcm^{-2} under occasionally vertical pressure and discharge activities. The exchanging vitality produced from nanogenerators can be utilized to charge a capacitor and light up a red light-transmitting diode through an extension rectifier. This outcome inventively grows the attainability of halide perovskites for function in a broad assortment of superior vitality collecting gadgets.

7.6. What Could Happen in the Future of Halide Perovskites?

The future of halide perovskites should answer three challenging issues i.e. 1) will perovskite solar cells achieve new breakthroughs beyond their current status of performance? 2) Will the future mass production and commercialization of these types of materials achieve the three ultimate goals of materials for optoelectronic applications: energy competent, low cost, and environmentally friendly? 3) Will the currently proposed new framework of single and double perovskite materials achieve enough efficiency like the efficiency of $CH_3NH_3PbI_3$ perovskites with improved stability and toxicity free new research horizon? So that the commercialization and production processes become more economical, sustainable, and environmentally friendly and its application may be realizable too. With these in mind, our question “what will be the future of these materials?” and “will their commercialization and mass production successful in the future with the expected performance or not?” are very important that everyone shall consider and dig for better development and application of the filed. What we believe is the future development of halide perovskites is promising because of the high power conversion efficiency and wide range applications raised from its structure property and simple synthesis and fabrication procedures for mass production. From all most challenges that must be considered are the toxicity of lead and moisture degradation of the organic cage. Because of these two reasons there are doubts whether to eliminate halide perovskites or repair them to be commercialized well is still in progress.

The big doubt is due to the release of lead toxic metal from industrial effulents as shown in Scheme 8. Furthermore, we hope that the commercialization of perovskite solar cell will be practical but (i) high stability and long lifetime, and (iv) low toxicity, (ii) controllable thin film deposition and growth, (iii) scalable and reproducible process must be realized prior to commercialization.[239,240] There are strategies to eliminate and/or minimize the bilogical effect of lead metal released from lead halide perovskite solar cell. **1) Chemical replacement strategy**, which is responsible for the development of lead free halide perovskite solar cells.[241–244] **2) Lead detoxification strategy** is the second one that can minimize toxicity of halide perovskites.[245–247] 3) **Chelation strategy,[248]** which is responsible to apply coordination bonding of organic molecules with lead metal to remove from industrial effluents during mass production of halide perovskites solar cells. 4) **Lead uptake by plants strategy,**[249] which applies plants to uptake lead metal released from the industrial effluents during manufacturing of lead halide perovskites. Plants are selected to store lead metal inside by absorbing it from the soil. This prevents the pollution of agricultural land from being polluted by lead released from industrial effluent. **5) Antioxidants strategy,[250]** which is implemented by making reactive oxygen species interacting with lead ion.



Scheme 8. Schematic diagram of the release of toxic lead from industrial effluents during commercialization. Reproduced with permission.[251] Copy right 2019, Royal Society of Chemistry.

The most important application of halide peroveskite materials is photovoltaic[252] and are superior in this application.[253,254] To realize this truth, the stability issue shall be improved to the extent that it can give confidence of practicing. Moreover, perovskite-perovskite tandem solar cell is reported as promising cell for large scale production.[255] Besides, $MASnI_{3-x}Br_x$ based perovskite tandem solar cell with power conversion efficiency of 30.7% is reported, overcoming the toxicity problem of perovskite solar cells.[256] Many works also reported the path towards enhanced stability for commercialization by using strategies such as **encapsulation**,[257–262] **chemical replacement approach**[262–265] and **protective layers**[266–272] **such as** molybdenum oxide, vanadium oxide to protect exposure from oxygen, moisture, high temperature and sunlight exposure,[273] fabrication of perovskite tandem solar module[274–281] while others stated scalability of module efficiency, achieving durability and stability, and process control, yield, etc. of manufacturing are vital for practical validations.[239] there are different strategic choices to enhance efficiency of peroveskite solar cells: **monolithic single junction solar cell**,[4] **Tandem peroveskite solar cell**,[280,282] **quantum dot solar** cell[283–288] and **metal nanoparticles with Plasmon effect** deposited on the photoactive surface induced metalized perovskite solar cell.[204,205,289,290] These possibilities are developed to overcome the limit that rapid growth of perovskite solar cell lacks suitable charge selective contacts.[291] Implementing Tandem perovskite solar cell is aimed to enhance power conversion efficiency compared to single junction perovskite solar cell though it retain low cost of manufacturing.[292–294]

As shown in Figure 14a the bifacial tandem solar cell absorbs both the direct sunlight and albedo light. While the bifacial single junction peroveskite solar cells work under front irradiation and only rear illuminations, the bifacial tandem solar cells work from illumination from both sides. If illuminated from only one side there happen large current mismatch among the subcells. Figure 14b shows the scanning electron microscope image of all-perovskite tandem solar cells with embedded structure of light trapping properties of the device architecture. Figure 14c indicates increased external quantum efficiency (EQE) due to the light trapping structure obtained from front illumination while Figure 14d indicated illumination from the rear side. Figure 14e shows the J-V curve obtained from the bifacial tandem solar cell and Pb-Sn cell. Figure 14f shows the stability of efficiency (29.3%) up to 100 seconds obtained from the Tandem solar cell under illumination with 30% of albedo light.

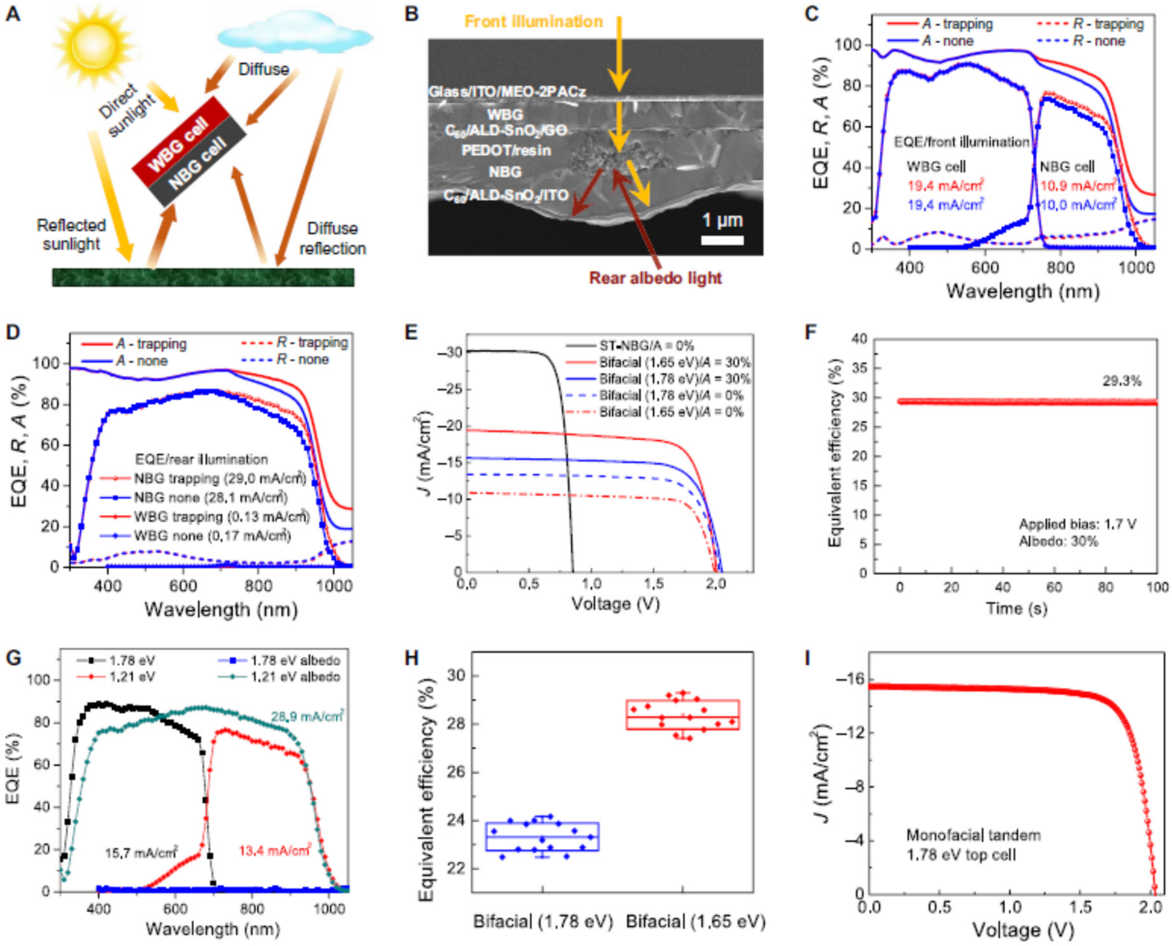


Figure 3a-i. Performance of bifacial all-perovskite tandem solar cells with embedded light-trapping structure. Reprinted with permission.[280] Copy right 2022, American Association for the Advancement of Science.

The bifacial tandem all provskite solar cells give EQE curve under front illumination and rear-side albedo light as shown from Figure 14g. Equivalent efficiency and J-V curve are indicated by Figure 14h-i. All these reliable data are great indications of illumination from both side induced Performance of bifacial all-perovskite tandem solar cells with embedded light-trapping structure. From these results, bifacial tandem solar cell is an excellent alternative for commercialization of peroveskite solar cell. This bifacial tandem solar cell also requires encapsulation for long term stability during practical application.[280] This tandem structure gives increased efficiency as shown in Figure 14f.

Tandem perovskite solar cell to be comercializable it requires to confirm thermal, moisture, oxygen and light stability.[295–299] In order to solve all these concerns, coordinationengineering and coordination chemistry of the various organic and inorganic halid materials structure forming both single and double perovskites with their related electronic interactions should be carefully studied. Moreover, the strategic coordination engineering frameworks stated in this review article (section 3) should get especial attention.

Another wondering thing in these halide perovskite materials that make them possible for future development is their wide range new applications! It is highly applicable in photovoltaic devices to meet the aim of energy demand, electronic devices such as lasers, photodetectors, phototransistors, LED and nonlinear emission sources to meet the goal of optoelectronic engineering, such as efficient water, CO_2 and HX splitting to meet photocatalytic goals, energy storage devices such as battery, and in efficient catalysis in order to achieve the purpose of halide reservoirs.

After all, which field of study is not enjoying with the application of these highly essential materials? Since halide anions are excellent redox mediators, halide perovskites may also be important in fields of membrane and reaction engineering due to their ability as halide reservoir. Moreover, they can be useful to reduce global warming by reducing and splitting CO_2. On the other hand, if we rise applications in biological system and life science in addition to the physical and chemical sciences: Growth of microorganism which need materials that can absorb light at infrared and near infrared regions, halide perovskites fulfill this criterion. But the lead atom is toxic and may affect the growth of microorganism. Other environmentally friendly metal atoms, which could be important to achieve this goal, should replace this toxic metal atom. On another account, being toxic should also be important for some reasons. For instance, it would also be wondering that if halide perovskite materials are applicable for agricultural aspects such as pesticides for killing some insects and organisms since lead atom is toxic, indicating that halide perovskites are not only used as halide reservoirs but also toxic metal such as lead metal reservoirs.

8. Concluding Remarks

The halide perovskite field is fast growing research area with improved device efficiency and the photophysics properties for wide range applications, but less stable. Consistently imperative research themes which have not been getting more attention are fundamental understanding of the coordination chemistry and coordination engineering as well as electronic interactions forming the halide perovskite structures in addition to their photophysics properties. Generally, grasping these fundamental concepts is quite relevant in five main concerns of this field: 1) stability improvements, 2) toxicity reduction, 3) discovery of new materials with multifunctional property, 4) remarkable semiconducting properties and performance improvements and finally, 5) realizing the existing and new potential applications of halide perovskite materials in practice. All these enhancements take place as a result of the modifications at either A, B or X sites and modifications at all A, B and X sites.

1) Stability improvement as a way for flexible practical applications: currently, this is the first challenge that blocks practical applications of halide perovskites materials. This limitation is not only for device but also the material itself is easily prone to degrade. As a key parameter for any optoelectronic applications, materials environmental stability and durability determine the lifespan of the device. Hence, in depth sympathetic of the chemistry and engineering of halide perovskites is helpful to enhance stability in two ways: a) enhancing the hydrophobic character of halide perovskites to overcome the solubility and dissolution of these materials. This can be done by increasing the carbon chain in the organic tail to reduce its hydrophilic character or to increase inorganic character of the halide perovskites by completely replacing $CH_3NH_3^+$ by water resistant in metal atoms such as Cs, Rb, etc. Using stoichiometric composition engineering of the organic tail with smaller amount of the organic tail could also enhance the hydrophobicity of these materials. b) Coordination engineering framework of halide perovskite structure that can overcome the stability issues in these materials.
2) Toxicity reduction for mass production of halide perovskites: Toxicity is the second most challenging issue that hinders the commercialization and mass production of halide perovskites. Understanding the chemistry and engineering of halide perovskites is highly relevant to partially or completely avoid the toxicity in these materials. This can be done by a) complete removal of lead atom and replacing it with environmentally friendly metal atoms such as Ti, Sb, Bi, etc. b) completely replacing lead atom by at least less toxic metal atoms such as Sn and Ge, which could not affect the environment significantly. c) If both mechanisms may not be successful, mixing metal ions can be the least alternative to optimize the degree of toxicity in lead based halide perovskites. d) If all these modifications may not be successful, engineering other perovskite materials with new framework and new stoichoimetric composition as well as structure could be the least alternative to avoid toxicity.
3) Enhanced semiconducting properties such as optical and electrical properties as well as efficiency enhancement. This basic intention of coordination chemistry and coordination engineering of halide perovskite materials is to improve optical and electrical properties and to design new material with better semiconducting properties for better performance.

4) Another exciting behavior of halide perovskites is their wide range potential applications resulted due to enhanced semiconducting properties that may be benefited from and require the fundamental concepts of chemistry and engineering in addition to their photophysics properties: It is wondering that halide perovskites are highly applicable beyond photovoltaic applications, for instance, a) many optoelectronic devices such as laser, LED, photodetectors, transistors and nonlinear emission sources, b) photocatalytic activities such as efficient water, CO_2 and HX splitting, c) storage devices such as active materials for LIB and Na ion battery as well as halide reservoirs for catalysis purpose. Moreover, discovery of new perovskite materials with multifunctional property and improved semiconducting properties: this point of view may be important to fabricate new device that fulfill the 'Triple E' rule: efficient, economical and environmental friendly solar cell device.

Finally, in order to provide direction in to the future continuity of this field, we have drawn a great concern: 'what will happen in the future of halide perovskites?' Would the new approaches, coordination chemistry and coordination engineering of halide peroivskites, bring new research horizon for the future or not? This concern indicates the future fighting among the challenges and promising opportunities of halide perovskite materials i.e. will this field stop or realized in the commercial enterprises and industries so that the future energy applications become powered by these materials. Moreover, this concern may also be important to draw new predictions on this field.

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