Strategies to Extend the Lifetime of Perovskite Downconversion Films for Display Applications

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Metal halide perovskite nanocrystals (PeNCs) have outstanding luminescent properties that are suitable for displays that have high color purity and high absorption coefficient; so they are evaluated for application as light emitters for organic light-emitting diodes, light-converters for downconversion displays, and future near-eye augmented reality/virtual reality displays. However, PeNCs are chemically vulnerable to heat, light, and moisture, and these weaknesses must be overcome before devices that use PeNCs can be commercialized. This review examines strategies to overcome the low stability of PeNCs and thereby permit the fabrication of stable downconversion films, and summarizes downconversion-type display applications and future prospects. First, methods to increase the chemical stability of PeNCs are examined. Second, methods to encapsulate PeNC downconversion films to increase their lifetime are reviewed. Third, methods to increase the long-term compatibility of resin with PeNCs, and finally, how to secure stability using fillers added to the resin are summarized. Fourth, the method to manufacture downconversion films and the procedure to evaluate their reliability for commercialization is then described. Finally, the prospects of a downconversion system that exploits the properties of PeNCs and can be employed to fabricate fine pixels for high-resolution displays and for near-eye augmented reality/virtual reality devices are explored.

1. Introduction

Solution-processed lead halide perovskite semiconductors are novel photovoltaic materials; in just 10 years, research into their use in photovoltaics has increased power conversion efficiency from 3.8% to 25.7%.[1] These semiconductors also show great promise as photonic sources in the form of nanocrystals (NCs) that are colloidally synthesized in a reactor or in situ during film formation.[2,3] Ever since identification of their applicability for these purposes in 2014,[4–6] metal halide perovskite nanocrystals (PeNCs) have received great attention for their narrow-band emission that is easily tunable over the visible spectral range, and for their high photoluminescence quantum yield (PLQY) even in the particle-size regime that exceeds the quantum confinement size (i.e., exciton Bohr diameter).[5–10] Passivation and device engineering have enabled external quantum efficiency of single-junction PeNC light-emitting diodes (LEDs) to approach 23.4–28.9%,[3,11–13] which is comparable to those of the state-of-the-art organic LEDs and CdSe quantum-dot (QD) LEDs. PeNCs have low crystal-formation energy and high tolerance to intrinsic defects,[9] so high-quality PeNCs with outstanding optical properties can be prepared free from passivation shells at room temperature, even without protection using inert gas.[14,15] This ease of preparation may allow for scale-up and low-cost preparation of high-quality PeNCs. These luminescent and technological advantages make PeNCs promising emitters for displays that have high efficiency, high color purity, and wide color gamut (**Table 1**). In addition, high absorption coefficient and near-100% PLQY

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Table 1. Summary of physical and optical properties of perovskite, semiconductor nanoparticles, and conventional inorganic phosphors.

Items	YAG:Ce	CdSe based	InP based	Perovskite
Structure	Microsized powder	Quantum dot (QD)	QD	QD, nanocrystal, bulk
	Cerium yttrium aluminium garnet	Core–shell, alloy, gradient	Core–shell, alloy, gradient	Compound core
	–	Covalent character	Covalent character	Ionic character
Synthetic temperature (°C)	>900	200–300	200–300	0–200
Peak range (nm)	550	460–640	470–640	450–780
PLQY (%)	≈90	≥90	≥90	≥90
FWHM[a)] (nm)	70–90	20–40	32–50	15–25
Molar absorption coefficient (cm^{-1} μM^{-1})	–	2–10[16]	1–5[17]	10–50[18]
Processability	Poor	Solution-processable, patternable	Solution-processable, patternable	Solution-processable, patternable

[a)] Full-width at half-maximum.

endow lead halide PeNCs with high color-conversion efficiency, so when PeNCs are used in a down-conversion layer, it can be very thin. This feature facilitates fabrication of very fine patterns for high-resolution displays and for near-eye augmented reality (AR)/virtual reality (VR) devices.

However, PeNCs are chemically susceptible to damage by light, heat, moisture, oxygen, and polar solvent,[19] so they degrade during purification using solution processes[20] and in subsequent storage. They also undergo phase segregation/aggregation and luminance decline when illuminated.[21] These instability problems severely limit the commercialization of PeNCs and devices that use them. The instability of PeNCs mainly stems from their intrinsically soft ionic lattice and loose binding between the PeNC core and the surface ligands. Therefore, commercialization of next-generation vivid displays that exploit the excellent optical properties of PeNCs requires development of ways to maintain their structural integrity.

So far, various strategies have been proposed to protect the optical performance of PeNCs from degradation by light, heat, moisture, oxygen, or polar solvent (**Figure 1**). Similar to typical nanomaterials, PeNCs also have a high specific surface area, so easy-to-form surface defects (uncoordinated atoms) can act as adsorption sites for oxygen or water molecules, which trigger the degradation of perovskite lattice.[22,23] In order to heal such defects, defect engineering was performed via surface defect passivation or fabrication of core–shell heterostructures (Figure 1A), which can simultaneously promote the photoluminescence efficiency and stability of PeNCs.[14,24] In addition, replacement of widely used alkylamine ligands, which bind loosely to PeNC surface, is an alternative pathway to improve colloidal stability of PeNCs (Figure 1B). Didodecyl dimethyl ammonium bromide (DDAB),[25] dodecylbenzenesulfonic acid,[26] zwitterionic ligands,[27] chelating diamine,[28] and cross-linked polymeric ligands[29] have been proven as better ligand candidates in terms of realizing the long-term colloidal stability. However, to realize the commercialization of PeNC-based color converter, PeNCs should maintain robust luminescence under very harsh conditions (e.g., high-flux blue light; 60 °C and 90% relative humidity (RH), etc.). Therefore, additional protection should be made on PeNCs. Encapsulating PeNCs with inorganic or organic polymers,[30–32] glass matrix,[33] or metal oxide[34] have been demonstrated as efficient methods to protect PeNCs from ambient-induced degradation (Figure 1C). Additionally, introduction of functional additive (e.g., free radical scavenger, thermally conductive boron nitride (BN)) into matrix-stabilized PeNCs could further improve their operation stability (Figure 1D).[35,36] During the past few years, a series of advances have been made in stabilizing PeNC emitters. Several start-up companies around the world are also investing in the development and commercialization of PeNC-based displays, which requires us to adopt standardized reliability assessment to promote the commercialization.

In this review, we systematically summarize recent progress on stability improvement of PeNCs for downconversion displays, then present their current commercialization status. We begin by describing the basic structure, synthesis methods, and surface properties of PeNCs. We then describe strategies to increase the chemical stability of PeNC emitters (**Figure** 1), including: 1) surface defect engineering, 2) use of core–shell heterostructures, 3) ligand engineering, 4) encapsulation engineering, and 5) functional additive engineering. We then introduce methods to coat PeNC film, and conditions to test the reliability of downconversion films to assess their compatibility with commercialization. We follow with a discussion of downconversion PeNC displays, including large liquid crystal display (LCD) TVs and VR/AR displays. We close with perspectives for commercialization of PeNCs as emitters in next-generation display materials.

2. Perovskite Nanocrystals

2.1. PeNC and Its Surface Structure

Perovskites have a corner-sharing octahedral structure with general chemical formula ABX_3 (**Figure 2**A), where the "A" site is a cation, which can be an organic ammonium (e.g., methylammonium (MA^+), formamidinium (FA^+), guanidium (GA^+)) or alkali metal (e.g., Cs^+), the "B" site is another cation, which can be a center transition metal (e.g., Pb^{2+}, Sn^{2+}), and the "X" site is a halide anion (e.g., Cl^-, Br^-, I^-).

PeNCs have their high PLQY (near unity),[37,38] narrow emission bandwidth (20–25 nm),[2] and strong absorption (10–50 cm^{-1} μM^{-1}),[16] so they are suitable as phosphors for color

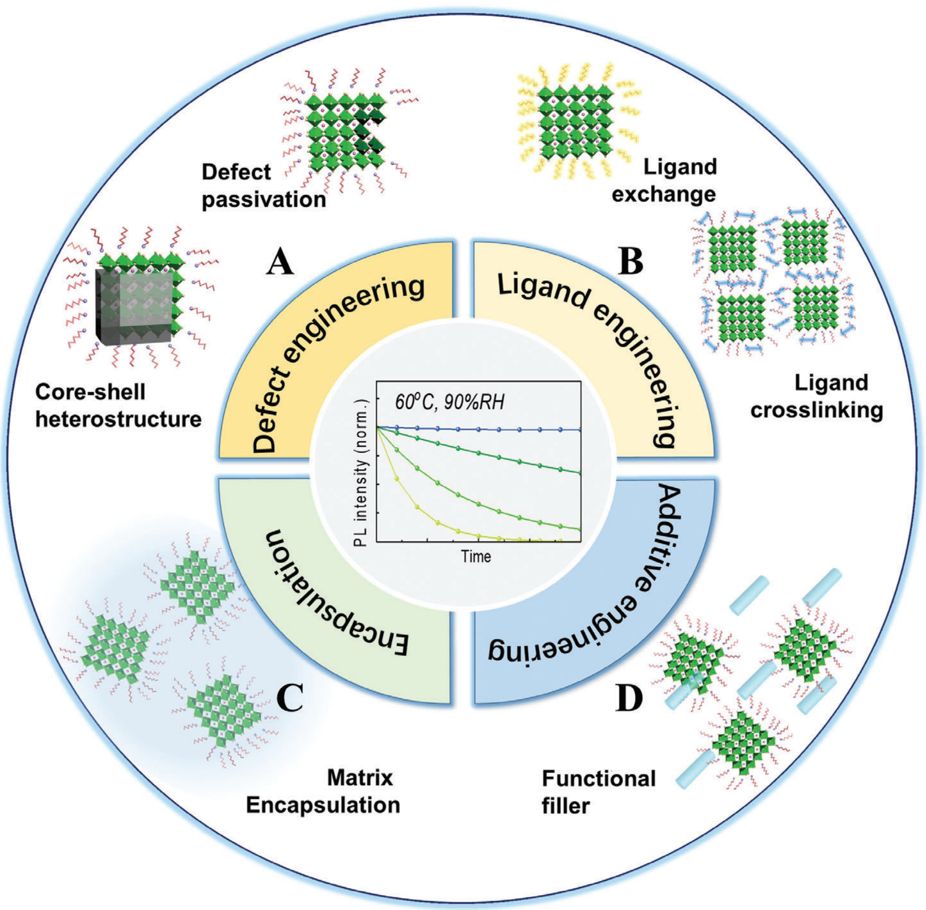

Figure 1. Strategies to increase the stability of metal halide PeNCs in downconversion films. A) Defect engineering with defect passivation and core–shell heterostructures to hide defects from the environment. B) Ligand engineering with ligand exchange and ligand cross-linking to smooth the dispersion of PeNCs in solvent and to inhibit diffusion of chemicals (e.g., H_2O, O_2, components of PeNCs). C) Encapsulation with matrix (organic or inorganic) polymers to slow inward and outward diffusion of chemicals (e.g., H_2O, O_2, components of PeNCs). D) Additive engineering using functional fillers.

downconversion.[2] QDs are crystalline particles that are smaller than the exciton Bohr diameter.[10] Small particles of such small size are unstable due to their large specific surface area, so they are not suitable for use as light downconverters in various environments. To suppress the size-dependent quantum-confinement effect and to achieve long-term stability, PeNCs that have diameters of ≈15 nm are being studied.[2,10]

Organic ligands are bound to the surface of a PeNC to allow particles to be dispersed in solutions. The bonding of PeNCs to organic ligands forms a dynamic equilibrium state by repeated formation and rupture of the bonds (Figure 2B).[8]

2.2. Typical Methods to Synthesize PeNCs

PeNCs can be synthesized by several pathways.[39] This section summarizes some of the most important ones.

Hot injection (**Figure 3**A) is a traditional method to synthesize CdSe QDs. $CsPbX_3$ (X = Cl, Br, I) is a commonly used PeNCs that has excellent thermal stability; it is synthesized at high temperature. Cation precursors (AX) give A^+ cations when dissolved in the solvent. Cation precursor solution is injected into hot solution containing solvent, ligands, and metal halide (MX_2). When the growth of PeNC reaches a target size, the reaction vessel is cooled with ice bath to quickly stop PeNC growth (Figure 3A). $CsPbX_3$ PeNCs are usually prepared with hot injection method[7] and tend to be used under higher temperature,[40] compared to PeNCs prepared using room-temperature synthesis method. Although MA^+, FA^+, GA^+ can form PeNCs, they have been reported less frequently than of NCs composed of perovskites that include Cs^+. $CsPbX_3$ PeNC has been known from the early stage of PeNC study, and there are a lot of research on the materials, optical physical properties, and their applications. In addition, the material is known to be mainly synthesized at high temperatures, and as a result, when exposed to heat, it shows more stable behavior at high temperatures than PeNCs with other ammonium cations (MA^+, FA^+, GA^+). It can be explained that Cs^+ is smaller than other ammonium cations, has a single point of charge, and has a smaller tolerance factor, resulting in a stronger crystal and more stable behavior at high temperatures.

When perovskite precursors are mixed at room temperature, bulk perovskite forms. By controlling the contact between these precursors with organic ligands, PeNCs can be obtained.

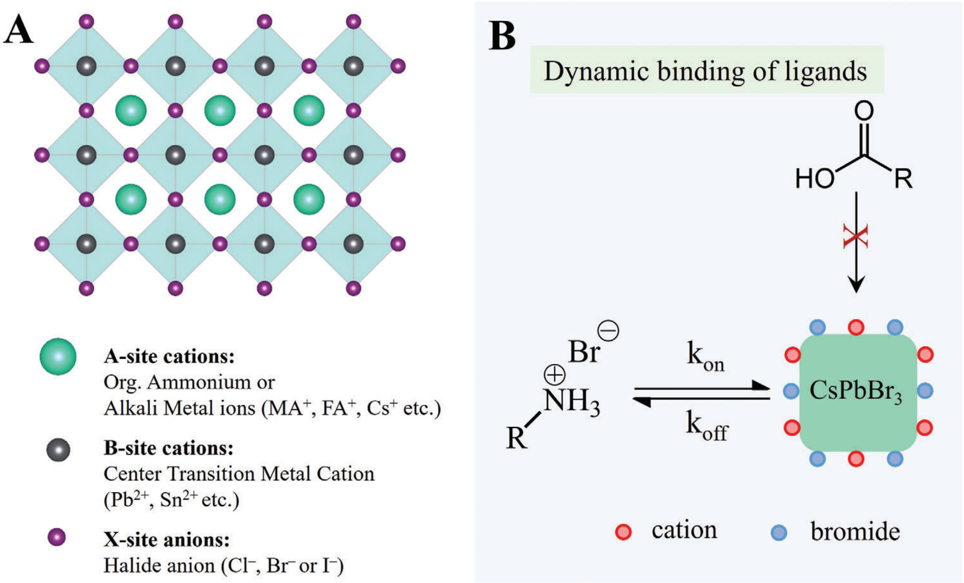

Figure 2. The crystal structure of a PeNC and the stabilization of the surface by organic ligands. A) Crystal structure of ABX_3 (A-site cations: organic ammonium (e.g., MA$^+$, FA$^+$, GA$^+$) or alkali metal (Cs$^+$); B-site cations: Center transition metal (e.g., Pb^{2+}, Sn^{2+}), X-site anions: halides (e.g., Cl$^-$, Br$^-$, I$^-$)).[2] B) Structure of ligands on PeNC surface, and dynamic equilibrium between PeNC and ligand. A) Reproduced with permission.[2] Copyright 2020, Wiley-VCH. B) Reproduced with permission.[8] Copyright 2016, American Chemical Society.

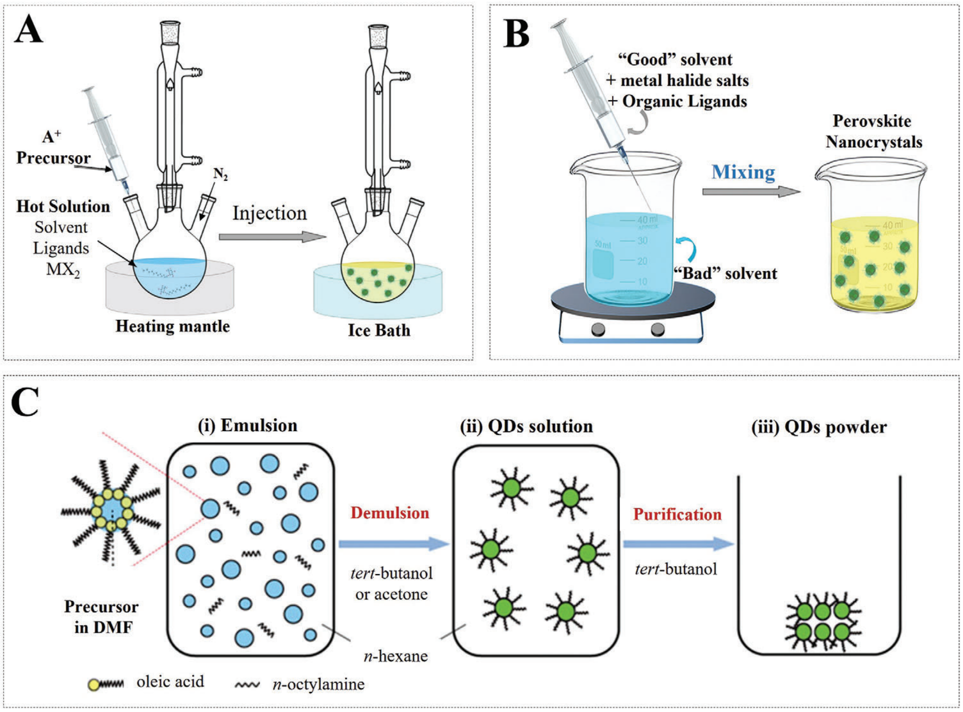

Figure 3. Three typical methods to synthesize PeNCs.[39] A) Hot injection method, in which precursor solution at room temperature is injected into a high-temperature precursor solution. B) Ligand-assisted reprecipitation (LARP) method, in which antisolvent is injected into precursor solution mixture of AX and BX_2 to obtain PeNCs in the presence of organic ligands. C) Emulsion method, in which a DMF/hexane solvent/antisolvent pair is agitated to form emulsion drops with perovskite precursors including organic ligands, then 3-butanol (*tert*-butanol) as a demulsifier is injected to break emulsion drops; this step leads to formation of PeNCs. A–C) Reproduced with permission.[39] Copyright 2019, American Chemical Society.

Ligand-assisted reprecipitation (LARP) synthesizes PeNCs by reprecipitation in the presence of organic ligands (Figure 3B). The *N,N*-dimethylformamide (DMF)–toluene pair is commonly used to precipitate perovskite from the mixture solution of precursors. When this solution includes organic ligands, bulk perovskite growth is inhibited, so nanometer-sized light-emitting PeNCs form.

The emulsion method is used to induce a DMF–hexane pair to form an emulsion (Figure 3C). Precursors for perovskite are confined to a limited-volume emulsion drop. When a demulsifier (e.g., *tert*-butanol) is added to a DMF–hexane emulsion that includes perovskite precursors, the emulsion drops break and yield perovskites that have limited size and that are coated with organic ligands. LARP and emulsion methods are generally used to prepare organic–inorganic hybrid PeNCs.

2.3. The Origins of the Instability of the PeNCs and Their Solution

Many approaches[2,11,41–43] have been tested to increase the photostability and thermal stability of PeNCs by improving their physical characteristics and by improving the surrounding matrix. The known problems in PeNCs are: 1) dynamic equilibrium between particles and ligands, 2) particle-surface defects, 3) ionic bonds, and 4) low crystallization energy.

The particle–ligand dynamic equilibrium means that the ligand attached to the surface of the particle does not form a strong bond that does not break. This condition means that the ligand repeatedly attaches to and detaches from the particle's surface (Figure 2B).[8] This phenomenon is observed between PeNCs and ligands attached to their surfaces.

The surface defects of PeNCs greatly affect their chemical stability. PeNCs are nanometer-sized crystals that have both surface defects and internal defects. The surface defects are caused by the external environmental factors such as heat, moisture, light, and polar solvent.[19] After surface defects form, they do not disappear naturally. PeNC is a crystal that is held together by ionic bonds. Its components are electrically charged, so they are strongly bonded to each other by electrostatic interaction, but H_2O molecules can attach to the PeNC surface and eventually dissolve it, to give defect sites on the PeNC surface.[44] Therefore, the crystal's luminescence rapidly decreases when it contacts water.

Many solutions to this problem have been suggested (Figure 1). Defect engineering is used to remove surface defects on the surface of PeNCs.[11,14,21,45–47] Ligand engineering is used to optimize surface ligand for dispersion in resin, and to control diffusion of chemicals and H_2O molecules.[25,29,48] Surface encapsulation can suppress chemical diffusion and halide release from the particle surface to the outside.[30,31,33,49,50] Use of functional additives such as fillers in the PeNC layer can improve stability and endow functions simultaneously.[35,51]

2.4. Downconversion Displays

Light downconversion in an LCD is a process of receiving blue light from the back-light of the LCD, transmitting some of the blue light, and converting the rest to green and red light, which sum spectrally to yield white on the display. Since the development of QD displays, many studies have been conducted on commercial-grade downconversion films.

PeNCs can be used in fields that use light-emitting QDs. Downconverting films that use perovskite and that are synthesized by the technology used to manufacture QD films can be inserted into LCD modules with blue backlight units to make optical downconversion displays.

PeNCs may be used instead of phosphor particles (Table 1). However, PeNCs are vulnerable to heat, moisture, and light, so for commercial applications the PeNCs must be protected from these factors in the environment.

Encapsulation is use of a protective surface layer on the PeNCs to isolate them from the external environment. Various organic or inorganic molecular encapsulants have been used. They include monomers, oligomers, or polymers. The encapsulant may bind directly to the PeNC surface with a Lewis base containing N, S, O, and P atoms, or may surround the PeNC surface by an interchain van der Waals interaction.[51–57]

Encapsulation that surrounds PeNCs is performed right after their preparation to improve their chemical stability and to improve their dispersibility in resin. To facilitate film formation, commercial resin is mixed with PeNCs and used to prepare a film by methods such as slot die coating. As-made film is processed to desired size and shape, then mounted on a display for downconversion display application.[2]

Downconversion-type LCD TVs (e.g., QLED TVs) that use a QD-enhancement film and an LCD module have been commercialized. However, reductions in their thickness are constrained, and they are expensive due to use of huge numbers of QDs. Accordingly, research and development of QD–organic light-emitting diodes (OLEDs) and quantum-dot electroluminescent (QD-EL) devices are underway to reduce the thickness of products and the usage of core materials, but only QD-OLED devices have been commercialized at the current level. Other technologies are being developed.

Several groups have reported the results of manufacturing large-area perovskite downconversion films and mounting them on displays.[2,58–63] Some companies that are striving to commercialize perovskite downconversion films have collaborated with LCD panel companies to disclose test production to the media.[64]

Stretchable displays are also being developed. A flexible and stretchable light downconverting layer has been prepared using perovskite light-emitting NCs and styrene–ethylene–butylene–styrene (SEBS) polymers, then linked to an EL device. The device performed downconversion normally even when stretched 100%; this result demonstrated the feasibility of developing stretchable perovskite light downconversion films.[65]

Light-emitting PeNCs also have applications in the AR/VR field. However, when thickness of QDs in optical downconversion displays for AR/VR using QDs, when the thickness of the QD film is reduced too far, blue light can leak through it and distort the color of the image on the display. Luminescent PeNCs can show better absorbance than previously commercialized QDs (i.e., CdSe QDs, InP QDs),[2] and can therefore solve this problem.[9,58] CdSe QDs,[66] InP QDs,[67] or PeNCs[8,16] are nanometer-sized particles that have an absorption coefficients that change according to the particle size (Table 1). PeNCs with a larger average particle size have a larger absorption coefficient, which is more advantageous for application to the light conver-

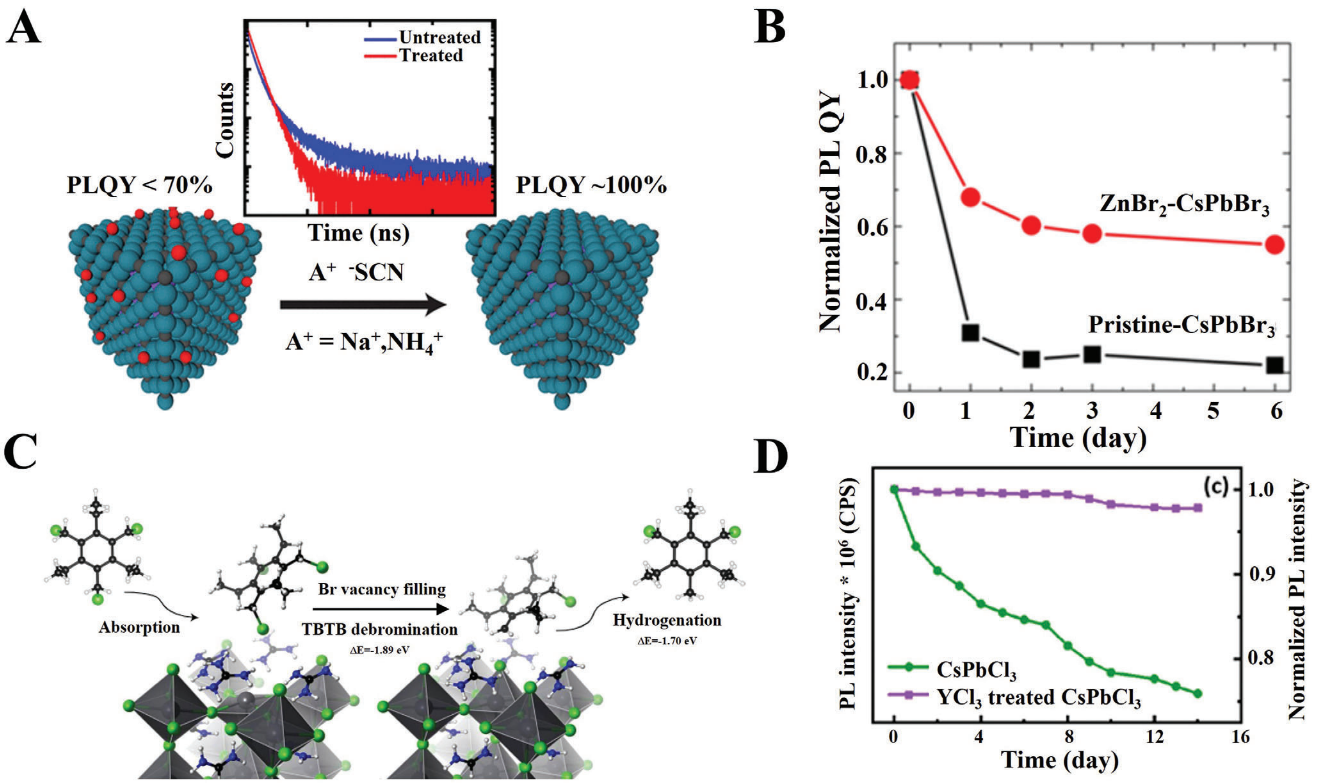

Figure 4. Examples of defect engineering. A) Defect passivation with strongly adhesive thiocyanate anion (SCN$^-$) ligand, leading to nearly 100% PLQY.[45] B) Defect removal with Br$^-$ anion in ZnBr$_2$.[14] C) Surface defect passivation with brominated single molecules.[11] D) Dual site surface passivation with YCl$_3$ achieves high PLQY. Positive and negative ions on a PeNC are stabilized at the same time when YCl$_3$ is used.[21] A) Reproduced with permission.[45] Copyright 2019, Royal Society of Chemistry. B) Reproduced with permission.[14] Copyright 2017, American Chemical Society. C) Reproduced with permission.[11] Copyright 2021, Springer Nature. D) Reproduced with permission.[21] Copyright 2018, American Chemical Society.

sion layer used in AR/VR. There are LED phosphors, but the size of the particles is micrometer region. It is difficult to use in an AR/VR device that uses a thin (<6 μm) light-conversion layer.

3. Strategies for Enhancing Stability of PeNC Downconversion Film

3.1. Defect Engineering

After synthesis of PeNCs, ligands can detach from their surfaces and thereby cause surface defects.[8] Once a defect has been created, the detached ligands sterically hinder access of free ligands to defect sites. The surface-area-to-volume ratio increases as PeNCs are scaled down, so the light-emitting property is sensitive to surface defects. In addition, because surface defects (uncoordinated atoms) can trigger the degradation of perovskite lattice upon adsorption of oxygen and water molecules thereon. Therefore, eliminating the surface defects is beneficial for both the optical properties and stability of PeNCs.

Uncoordinated Pb can be removed using a post-treatment method that uses thiocyanate anion (SCN$^-$) ligands, which can bond strongly with Pb. This method can perfectly passivate PeNCs with PLQY of 100% (**Figure** 4A).[45] SCN$^-$ bonds strongly with uncoordinated Pb moieties, and therefore increases light emission by removing them. Halides can be delivered to uncoordinated Pb as monomer or metal salt.

Halide vacancies can be quenched by using metal salts such as ZnBr$_2$ and AuBr$_3$.[14] For example (Figure 4B), ZnBr$_2$ can supply halide anion (Br$^-$), which forms an ionic bond with uncoordinated Pb, and thereby patches the trap site and increases photoemission. When AuBr$_3$ is added to CsPbBr$_3$, Br$^-$ from the AuBr$_3$ patches trap sites on the CsPbBr$_3$ surface and the green luminescence increases without significant shift in wavelength shift. In contrast, when AuCl$_3$ is used, the Cl$^-$ that it provides can replace some Br$^-$; this reaction causes a blueshift in the PL wavelength. The formation of mixed halide CsPb(Br/Cl)$_3$ indicates that the AlCl$_3$ can be effective Cl$^-$ donor to patch halide vacancies on the surface of PeNCs. The effect of treatment using AuX$_3$ can be turned off by the addition of ligands with thiol groups and turned on by the removal of ligands with thiol groups.[68]

Metal halides such as AlBr$_3$ can increase the PLQY of PeNCs during synthesis; use of metal halides to supply excess halides can reduce the number of halide vacancies in PeNCs.[19] Stable CsPbX$_3$ nanoplates have been synthesized by using AlX$_3$-DDT to induce anion exchange reaction in CsPbCl$_3$ nanocubes.[20]

Uncoordinated Pb can also be removed by using 1,3,5-*tris*(bromomethyl)-2,4,6-triethylbenzene to heal bromide vacancies (Figure 4C).[11] Br atoms in a molecular structure adhere to the uncoordinated Pb on PeNCs to remove the trap sites. Use of yttrium (III) chloride (YCl$_3$) can achieve extreme efficiency in this process (Figure 4D).[21] YCl$_3$ increases the luminescence of particles by removing trap sites in $CsPbCl_3$ at the sites of Pb–Cl ion pairs.[21]

In addition to post-treatment of PeNCs with various passivators, ionic doping has also observed as an efficient pathway to remove the nonradiative defects and increase the stability simultaneously.[69] Mn^{2+} doping greatly promotes the thermal and storage stability of $CsPbCl_3$ and $CsPbBr_3$ PeNCs.[70] Mn^{2+} doping can not only improve the PLQY of $CsPbCl_3$ PeNCs, but also enhance their lattice formation energy, thus resulting in improved colloidal stability of PeNCs against air and heat. Yb^{3+} doping endowed $CsPbCl_3$ NCs with strong emission of near-infrared 986 nm and very high PLQY of 127.8%, a factor of 25.6 times enhancement compared to that of pure $CsPbCl_3$ PeNCs (PLQY of 5.0%).[71] Yb^{3+} doping largely improves the T_{80} lifetime (time for the PL intensity to decrease to 80% of its initial brightness) of $CsPbCl_3$ PeNCs from 27 to 85 h under continuous irradiation with a 6 W UV (365 nm) lamp. In addition, Mg^{2+} and Ni^{2+} doping can also reduce the defects of $CsPbBr_3$ NCs and improve their PL efficiency and photothermal stability.[72,73]

Overall, defect passivators or ionic doping can improve the PL efficiency and colloidal stability of PeNCs to a certain extent, but these methods still cannot meet the stability of color conversion layer. It is still necessary to combine subsequent stabilizing strategies to further promote the PL stability of PeNCs under harsh conditions (60 °C, 90% RH test; high-flux test).

3.2. Core–Shell Heterostructures

Colloidal epitaxy to fabricate core/shell structure in traditional CdSe and InP QDs has been well established.[74,75] Epitaxy of shell that has a wider band-gap than the core semiconductor can both chemically protect it and confine excitons to it, and thus simultaneously increase the PLQY and photostability.[24] The binding of surface ligands is highly dynamic, and surface defects form easily,[8] so hetero-epitaxial shell growth can also effectively modify PeNCs to improve both their colloidal stability and PL efficiency. However, a method to achieve layer-by-layer epitaxial growth of a shell on perovskite QDs has not been achieved, because of the structurally soft and chemically labile nature of metal halide perovskites.[76,77] Nonetheless, several tailored synthesis methods have been tested as ways to prepare quasi-core/shell PeNC heterostructures with greatly increased stability.

Because of ionic structure and good match of the lattice with PeNCs, wide-bandgap halide perovskite-derived materials (e.g., Cs_4PbX_6, Rb_4PbBr_6, or $CsPb_2Br_5$) have been introduced to fabricate core/shell PeNCs.[46,78,79] The low formation energy of these ionic shell materials enables shell growth at low temperatures to avoid damage to the labile PeNC cores. For example, post-treatment with rubidium oleate (RbOA) can yield the $CsPbBr_3/Rb_4PbBr_6$ core/shell structure.[46] RbOA exchanges with surface monovalent Cs^+ cation and simultaneously triggers a phase transformation to form a 0D Rb_4PbBr_6 shell. After deposition of this shell, the average size of $CsPbBr_3$ PeNCs increased from 8.5 to 10.2 nm, and PLQY increased significantly from 40% to 85%. Importantly, the colloidal solution of $CsPbBr_3/Rb_4PbBr_6$ core/shell PeNCs retained >90% of the initial PLQY after 42 h of intense blue LED irradiation (450 nm, 175 mW cm^{-2}), whereas the classical CdSe/CdS QDs retained only 50% of their emission after 18 h of irradiation under the same condition (**Figure 5**A). The exceptional photostability may be a result of robust protection by the Rb_4PbBr_6 shell. $CsPbX_3/Cs_4PbX_6$ core/shell PeNCs have also been reported. $CsPbBr_3/Cs_4PbBr_6$ core/shell nanostructure confined the excitons to within the core and resulted in a much higher PLQY of 96.2% compared to the initial $CsPbBr_3$ seeds (85%), but stability data were not provided.[9]

PeNCs coated with ionic shells remain sensitive to moisture. To overcome this problem, poly(methyl methacrylate) (PMMA) and poly(ethyleneimine) (PEI) polymer ligands have been used to prepare $CsPbBr_3/CsPb_2Br_5$ core/shell NCs by using a mechano-chemical (ball-milling) synthesis method.[79] Multidentate polymer ligands strongly bound to the NC surface and endowed $CsPbBr_3/CsPb_2Br_5$ core/shell NCs with excellent water-resistance and good thermal stability.

Covalent metal chalcogenides have robust crystalline networks and semiconducting properties. Therefore, they are attractive as encapsulants of labile PeNCs. Classical core/shell QDs that use CdSe or InP have their large lattice-formation energy, so their preparation requires epitaxial growth of metal chalcogenide shell at a high temperature (200–260 °C) for >30 min,[74,75] which can lead to the fusion and phase transformation of PeNC seeds, and is therefore incompatible with soft-lattice PeNCs. Use of oleylammonium bromide (OAmBr) to synthesize $CsPbBr_3$/ZnS core/shell NCs can prevent the phase transformation of $CsPbBr_3$ seeds during the persistent heating process.[47] Also, zinc diethyldithiocarbamate ($Zn(DDTC)_2$) shell precursors slowly release Zn and S at a low temperature (120 °C); the low temperature of shell growth and slow release of precursor ensure both the stability of $CsPbBr_3$ seeds and prevention of separate nucleation of the ZnS impurity phase. The resulting $CsPbBr_3$/ZnS core/shell NCs had superior water-resistant stability and maintained intense luminescence for >2 d (Figure 5B). However, the ZnS shell is <2 nm thick and cannot be tuned; furthermore, the PeNC cores fused during the shell growth, so the average size increasing from ≈10 to >40 nm (Figure 5B).

CdS and PbS can be shelled or deposited on $CsPbBr_3$ and $CsPbI_3$ NCs by adopting different chemical protocols.[80,81] These chalcogenide-capped PeNCs showed improved chemical, thermal, and photostability compared to bare PeNCs. However, such structures were obtained by random deposition of chalcogenides on PeNCs without controllable 3D epitaxial growth. Despite the inhomogenous decoration of the PeNC surface with metal chalcogenides, these embryonic perovskite-centered core/shell NCs have shown greatly improved phase, thermal, and light stability, and thereby highlight the great potential of stabilizing PeNCs by using this type of core/shell heterostructure.

In addition, the core/shell structures can passivate the PeNC surface well and reduce phonon scattering and thus yield ultranarrow emission,[76] which is desired for light-emitting devices and essential for next-generation quantum light sources. Furthermore, epitaxial metal chalcogenide shells may eliminate electrically induced ionic migration and thus facilitate the construction of stable electroluminescent devices. All of these advantages of perovskite/metal chalcogenide core/shell structures motivate the development of a controllable pathway to fabricate such epitaxial core/shell heterostructures.

At least three possibilities could be explored: 1) *Ligand engineering*: ligands with strong binding energy to PeNC surface could

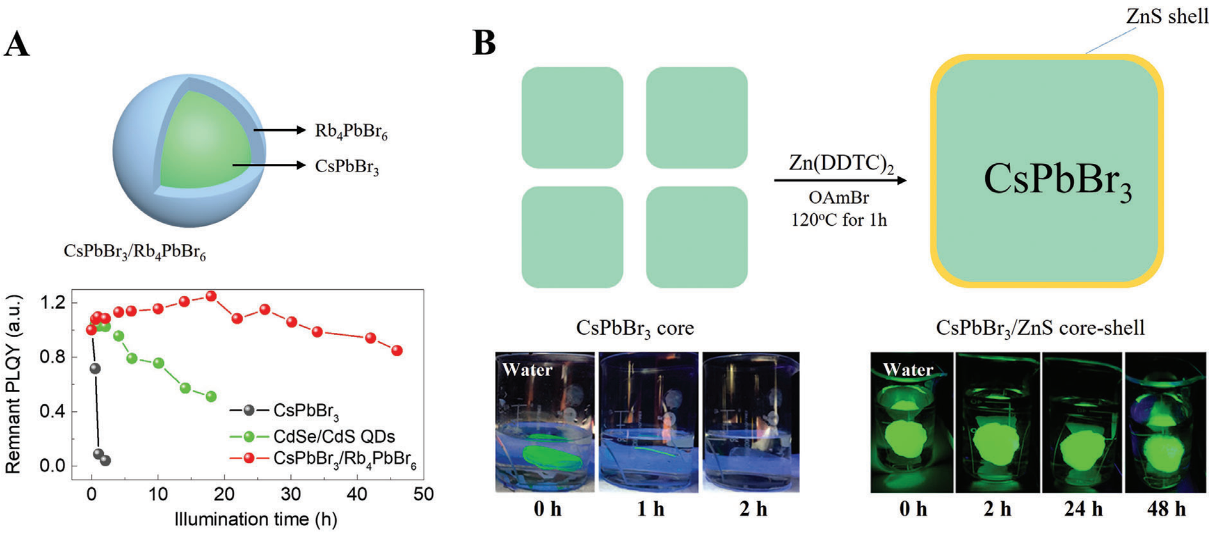

Figure 5. A) Schematic illustration of the $CsPbBr_3/Rb_4PbBr_6$ core/shell nanostructure, and photostability of $CsPbBr_3$ PeNCs and $CsPbBr_3/Rb_4PbBr_6$ core/shell NCs compared to a typical CdSe/CdS core/shell QDs. Reproduced with permission.[46] Copyright 2018, American Chemical Society. B) Schematic illustration of the formation process of $CsPbBr_3$/ZnS core/shell NCs. Shown below are the photos of the $CsPbBr_3$ and $CsPbBr_3$/ZnS core/shell NC films in water, excited with a 365 nm UV lamp. Reproduced with permission.[47] Copyright 2021, American Chemical Society.

be introduced to suppress their fusion or phase transformation during long-term high-temperature epitaxial growth.[27,28] 2) *Shell precursor engineering*: selection of precursors with high reaction activity can decrease the growth temperature and thus reduce thermal damage to PeNC seeds. In this case, the reaction temperature and injection rate of shell precursors should be carefully regulated to avoid secondary nucleation of shell materials. 3) *Facet engineering*: epitaxial growth is typically facilitated by using appropriate lattice matching at the interface. Most reported PeNCs are either cubes or platelets and have similarly exposed facets. Therefore, anisotropic facets of PeNCs may help epitaxial growth of chalcogenide materials.[77,82]

3.3. Ligand Engineering

3.3.1. Ligand Exchange

The photochemical stability of PeNCs can be increased using ligand engineering. In general, a PeNC consists of nanometer-sized perovskite crystals surrounded by organic ligands.[7,10,42,83,84] Organic ligands effectively passivate the surfaces of PeNCs to protect particles from the external environment and reduce the nonradiative recombination of spatially restricted electron–hole pairs in perovskite crystals.[85–90] Therefore, the PL efficiency of PeNCs can be greatly influenced by the binding of perovskite crystals and ligands, and the strengthening of the bindings can increase the chemical stability of PeNCs. The synthesis of traditional perovskite particles uses a combination of a ligand alkyl acid and an amine of PeNC.[7,10,83] However, proton transfer between carboxylic acid and ammonium ligands can be neutralized by Brönsted acid–base equilibrium to form carboxylic acid ammonium salt, which can be easily detached from the surface of perovskite crystals.[8,25,45,86]

An amine-free method to synthesize PeNCs can increase colloidal stability of PeNCs.[25,91] Octylphosphonic acid (OPA) may interact with the lead atoms of PeNCs, so the OPA-capped PeNC may maintain PLQY > 90%.[91] OPA-capped PeNC maintains a high PLQY after several purification processes; this indicates that the binding of PeNCs and ligands was strengthened. PeNCs with OPA as a surface ligand show significantly improved chemical stability during storage under ambient conditions due to strong PeNC–ligand binding.

A zwitterionic ligand, which supplies cations and anions at the same time and binds strongly to PeNCs, has been reported.[27] Strong ligand binding on a PeNC facilitates the dispersion of PeNCs in organic solvents without PeNC aggregation and precipitation.

Ligand replacement is a traditional method to disperse nanoparticles in various matrices. The PeNCs with oleic acids on the surface can be dispersed only in a nonpolar solvent such as hexane. When dispersed in polar epoxy resins, the particles aggregate, so a homogenously dispersed PeNCs–polymer composite cannot be formed. The simplest way to solve this problem is to attach ligands that bind strongly to the surface of an PeNC.[25] Use of DDAB to replace the original ligand (oleic acid or oleylamine) on the surface of $CsPbBr_3$ can increase the PLQY (**Figure 6**A).

In addition, polymer ligands with multiple binding sites can increase PeNC photoemission stability (Figure 6B).[29] When $CsPbI_3$ is used, the luminescence decreases and disappears due to a change in the crystal phase over time. Replacement of thiol with a ligand after purification can suppress this change and ensure luminescent stability.[92]

3.3.2. Ligand Cross-Linking

When a ligand detaches from the surface of a PeNC, a trap site is generated and reduces the luminescence of the PeNC. In general, PeNCs are surrounded by organic ligands;[7,42,83,84] they decrease the number of defect sites, and therefore reduce the nonradiative

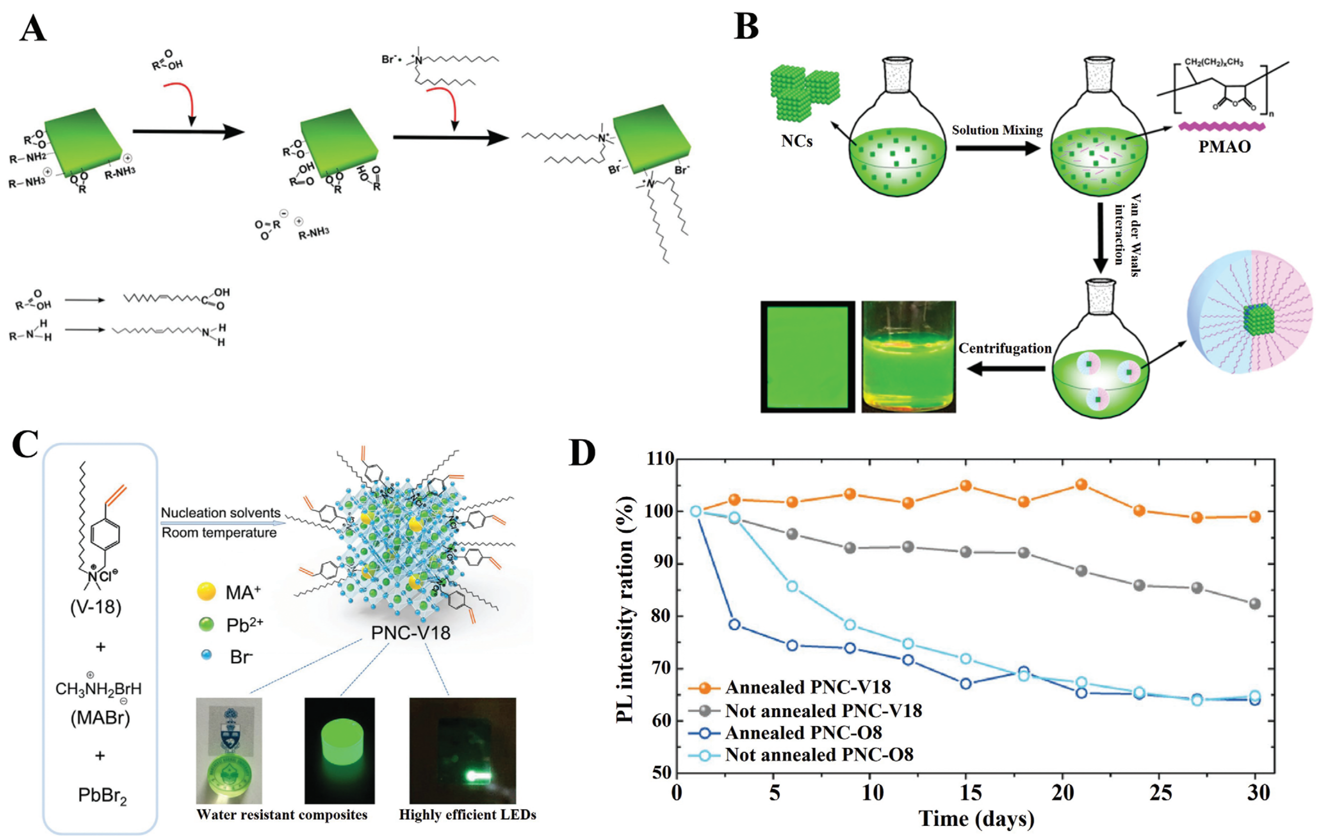

Figure 6. A) Single-molecular ligand replacement.[25] B) polymer-type ligand shell coating.[29] C) Ligand exchange with vinyl group ligand to induce cross-linking use of C=C bond. PNC = perovskite nanocrystals. D) Reliability results of (C). Annealed PNC-V18 sample is the most stable.[48] A) Reproduced with permission.[25] Copyright 2016, Wiley-VCH. B) Reproduced with permission.[29] Copyright 2019, American Chemical Society. C,D) Reproduced with permission.[48] Copyright 2017, Wiley-VCH.

decay at the time of hole–electron recombination in the PeNCs, and consequently increase their luminescence.

The bonding between the PeNCs and the surface ligand greatly affects the chemical stability of the particles. Oleic acid and oleylamine are used simultaneously in the synthesis of PeNCs.[7,10,83,84] In solution, these two easily form ammonium-carboxylate adducts by exchanging a proton on the surface of the PeNC, so the particle separates easily from the surface of the PeNCs and destabilizes them. The PeNCs from which the ligands are removed aggregate in the solution; this reaction causes a redshift and reduces luminescence.[8,25,45,91–93]

A reactive functional group can be introduced to the surface of PeNCs by mixing molecules with curable functional groups with perovskite precursors and reacting the mixture together.[94] This method has been applied using an S_N2 reaction on a vinylstyrene-derived ammonium salt. The coated PeNCs are prepared by adding this salt during PeNC synthesis, then mixing with methylmethacrylic acid (MMA) to give a photocurable resin (Figure 6C).[48] Heat treatment cross-links the ligands in the PeNC and MMA, and thereby encapsulates the polymer; this phenomenon suppresses material diffusion from the outside to the inside and thus greatly increases the stability of the particle (Figure 6D).[48]

3.4. Encapsulation Engineering

Encapsulation is the strategy of surrounding PeNCs with substances that do not directly react with the perovskite surface. This method can increase the photochemical stability of PeNCs. The characteristic of this approach is that it reacts only with the materials around the PeNCs. The PeNCs do not undergo a chemical reaction, so the simplest way to stabilize them is by wrapping them with nonreactive or weakly reactive polymers.[52,55,95]

PeNCs can also be mixed with reactive polymers and curing.[30,49,50,96] A monomeric rather than a polymeric ligand is introduced to generate a chemical reaction around the PeNCs, and the resultant PeNC–polymer composite surrounds the PeNCs to protect them from the environment.[48]

3.4.1. Reactive Matrix

If PeNCs are embedded in a metal oxide matrix, they may have more long-term reliability than those dispersed in other organic polymers.[52] Therefore, several groups have attempted to embed the PeNCs in a metal oxide matrix such as SiO_2,[30,49,50] TiO_2,[96] or ZrO_2.[97] However, the method of forming a metal oxide film

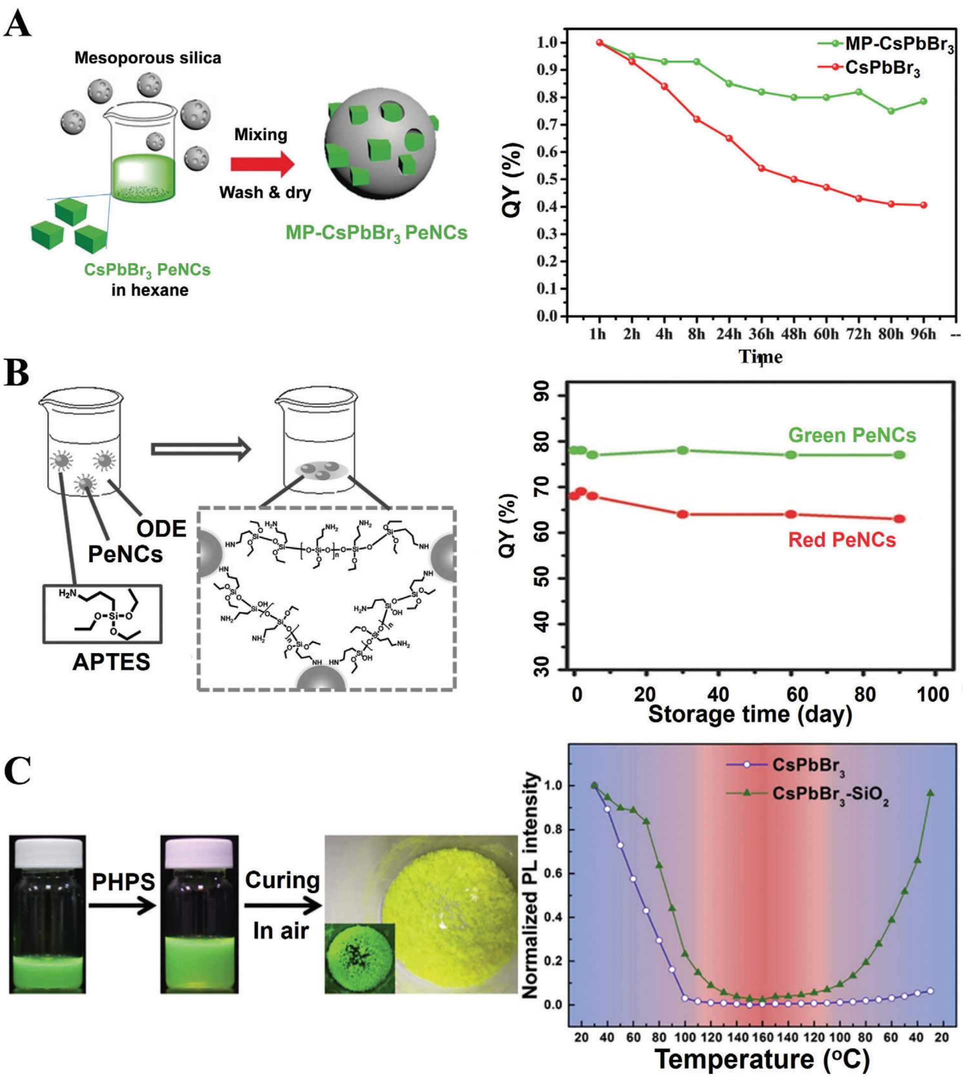

Figure 7. A) Synthesis scheme of mesoporous green-emitting PeNCs-silica nanocomposite (MP-PeNCs) and photostability test of MP-CsPbBr$_3$ and CsPbBr$_3$. Red line: photostability of CsPbBr$_3$ particles; green line: photostability of CsPbBr$_3$ particles loaded on mesoporous silica.[49] B) Schematic illustration of formation of PeNC–silica nanocomposites and PLQY stability of the PeNC-silica nanocomposites.[30] C) Synthesis procedure of CsPbBr$_3$ PeNCs-incorporated PHPS-derived SiO$_2$ nanocomposites and temperature-dependent PL intensities of CsPbBr$_3$ (blue open circle) and CsPbBr$_3$–SiO$_2$ composites (green solid triangle).[50] A) Reproduced with permission.[49] Copyright 2016, Wiley-VCH. B) Reproduced with permission.[30] Copyright 2016, Wiley-VCH. C) Reproduced with permission.[50] Copyright 2017, Elsevier.

on the surface of the PeNCs differs according to the material and conditions, so the conditions must be optimized.

PeNCs have been embedded in mesoporous silica.[49] A complex is produced during mixing (**Figure 7**A). CsPbBr$_3$ loaded into mesoporous silica has better photostability than bare CsPbBr$_3$.[49] CsPbBr$_3$ particles are loaded on mesoporous silica by mixing CsPbBr$_3$ solution with mesoporous silica, then removing the solvent.[98]

Particles can also be produced by introducing a perovskite precursor into mesoporous silica. PeNCs with a quantum confinement effect limited to the pore size formed inside a template,[99] and blue-emitting CsPbBr$_3$ PeNCs have been introduced into mesoporous thin films.[85]

SiO$_2$ can be deposited on the surface of the PeNCs by using an SiO$_2$ precursor and an organic silane compound (3-aminopropyltriethoxysilane (APTES)) as a ligand.[30] A precursor solution including APTES is prepared, PeNCs are prepared without atmospheric contact, and then moisture and organic silane in the atmosphere are brought into contact by atmospheric exposure to induce formation of SiO$_2$ on the surface of the PeNCs by a hydrolysis–condensation process.[100] Red-emitting and green-emitting PeNCs–SiO$_2$ are stable. After storage of 90 d, the PLQY of red-emitting PeNC–SiO$_2$ decreased <5%, and PLQY of green-emitting PeNC–SiO$_2$ showed almost no change (Figure 7B). This simple one-pot SiO$_2$ coating approach greatly increases the stability of PeNCs in ambient air.

Perhydropolysilazane (PHPS) has been used to form inorganic SiO$_2$ (Figure 7C).[50] Unlike organic silane compounds, PHPS induces formation of a pure SiO$_2$ layer during contact with humidity by giving off ammonia (NH$_3$). Inorganic SiO$_2$ shows better chemical stability, hardness, and high density, unlike organic silane APTES and SiO_2 that uses tetraethyl orthosilicate. The SiO_2 layer that is formed using PHPS is more resistant to moisture, heat, and chemicals than the SiO_2 layer obtained using organic silane. Remarkably, when inorganic SiO_2 is formed using PHPS, the original light-emitting characteristics are restored by raising the temperature then returning it to room temperature. This response occurs because the inorganic SiO_2 inhibits the change in the crystallinity of the particles from cubic to orthorhombic along with the deformation of physical properties due to heat.

Amorphous SiO_2 can be formed on the surface of PeNCs by using the sol–gel method,[101,102] and some authors have attempted to stabilize the surface using Al_2O_3,[34] TiO_2,[96] or ZrO_2[97] instead of SiO_2. PeNCs surface-coated with ZrO_2 are more stable than the uncoated PeNCs at room temperature and high humidity (60 ± 10%).[97]

PeNCs–polymer composite can be prepared by mixing PeNCs with a reactive resin; however, if the PeNCs-resin and the composite are not compatible, they do not mix with each other. As a result, the particles agglomerate rather than dispersing uniformly in the polymer, so the resulting PeNCs have inferior optical properties.[103]

A composite can also be produced by mixing silicone resin and PeNCs. Silicone matrix is formed by a hydrosilylation reaction using Pt as a catalyst.[104] Silicone matrix is hydrophobic and can slow H_2O diffusion around PeNCs in silicone matrix.

Films can be produced using a UV-curable acrylate binder (polyurethane-derived photopolymer (NOA 63)). Core–shell perovskite quantum dots (PeQDs) (red $CsPb(Br_{0.35}I_{0.65})_3/CsPb_2Br_5$ and green $CsPbBr_3/CsPb_2Br_5$) are chemically stable under UV irradiation, water, and high temperature of 100 °C. LCDs were produced using red and green PeQDs-containing color conversion films on top of blue backlight and achieved 100.5% color space of Rec. 2020.[105]

Thiol-ene chemistry has been applied for quick reaction, and a polyhedral oligomeric silsesquioxane (POSS) structure was introduced on the particle surface to solve the anion exchange. Anion exchange is a fast process and can be used to control emission colors for PeNCs with different halide anion addition.[106] Nearby halide anions can distort emission color of PeNC giving to undesirable emission color. It is necessary to prevent anion exchange between PeNCs and halide anions to maintain desirable emission. Encapsulation can slow halide anions diffusion to PeNCs and anion exchange.[107,108] POSS has been applied to an LED color conversion layer mixed with silicone resin.[109] $CsPbX_3$@glass composites were prepared by direct growth of PeNCs in the molten class. The $CsPbX_3$@glass composite was manufactured in a powder form, then covered with a polydimethylsiloxane (PDMS) film to increase chemical stability and ensure near-unity PLQY (**Figure 8**A).[33] The PL intensity changed little after 24 h of treatment in UV radiation (6 W) or after 7 d in 90 °C water (Figure 8B,C), and the PLQY was not changed even stored in air for 90 d. An LCD was manufactured by laying the film on top of a blue backlight; the color gamut was 103% of National Television System Committee (NTSC) and was 52% better than the original LCD that had a white backlight. The LCD with blue backlight operated for 48 h in a stability test and stably emitted blue/green/red mixed color white emissions, and retained almost 100% of its initial EL intensity.[33]

The PeNC precursors and polyvinylidene fluoride (PVDF) are dissolved in DMF simultaneously. The PeNC precursors–PVDF solution is coated on a substrate to form a PeNC film (Figure 8D).[31] As the solvent in the film evaporates, the PVDF crystallizes, then the PeNC precursor forms PeNCs. The color of emission can be controlled blue to red by adjusting the halide ratio in the PeNC precursor.

As another example, UV-curable siloxane resin was prepared using a Ba^{2+}-catalyzed nonhydrolytic sol–gel process in the presence of PeNCs. This siloxane resin has been applied to an LED (**Figure 9**).[32]

To prevent PeNC degradation due to moisture, siloxane oligomers can be synthesized from silanes by a nonhydrolytic sol–gel process in the presence of Ba^{2+} catalyst under inert condition. The PeNC–siloxane resin has been used in downconversion films for blue-emitting LEDs. Silanes with methacrylate functional groups and PeNCs having C=C bonds in alkyl chained ligands are introduced during the synthesis of siloxane oligomers. The methacrylate functional groups in siloxane oligomers and C=C bonds on the surface of PeNCs are connected to form crosslinked network during UV curing to form a C–C bonds. The C=C double bonds in surface ligands can also react with methacrylate group to form a more cross-linked and compact network (Figure 9A). Moisture greatly increased the photophysical properties of the perovskite PeNCs in various reliability tests (Figure 9B,C). H_2O molecules adhere to defect sites of PeNCs in the early stages of the reliability test and thus increase their luminescence (Figure 9D).

3.4.2. Nonreactive Matrix

The PeNCs are chemically labile when exposed to polar solvent, light, moisture, or heat,[19] so they are sensitive to chemical environment of encapsulated matrix. Therefore, when dispersed in various types of matrices, PeNCs may agglomerate or dissolve into it. To overcome this problem, encapsulation with organic or inorganic molecules has been used to protect particles from the environment. This encapsulation of PeNCs increases their stability in air and resistance to water to bare PeNCs. The encapsulation also improves the miscibility of PeNCs with the matrix so their dispersibility in it increases. Depending on the matrix, surface passivation can occur; when this happens, the PL of the PeNCs increases. Research is ongoing to increase the stability of PeNCs against moisture and oxygen by using polymers to encapsulate PeNCs.[52,54,57]

The polymer to be used for encapsulation must stabilize the luminescence of individual PeNCs and should not cause blueshift of PL due to dispersion of PeNCs in the matrix.[59] When the concentration of PeNC in polymer matrix is low, the PL shifts toward blue due to decomposition of the PeNC surface. When the concentration of PeNC particles in polymer matrix is high, the PL shifts toward red due to agglomeration and self-absorption of emitting light between PeNC particles. Such degradation-induced blueshift could be suppressed by encapsulation with polystyrene (PS), which performs much better than poly(methyl methacrylate) (PMMA). Molecular dynamics simulations

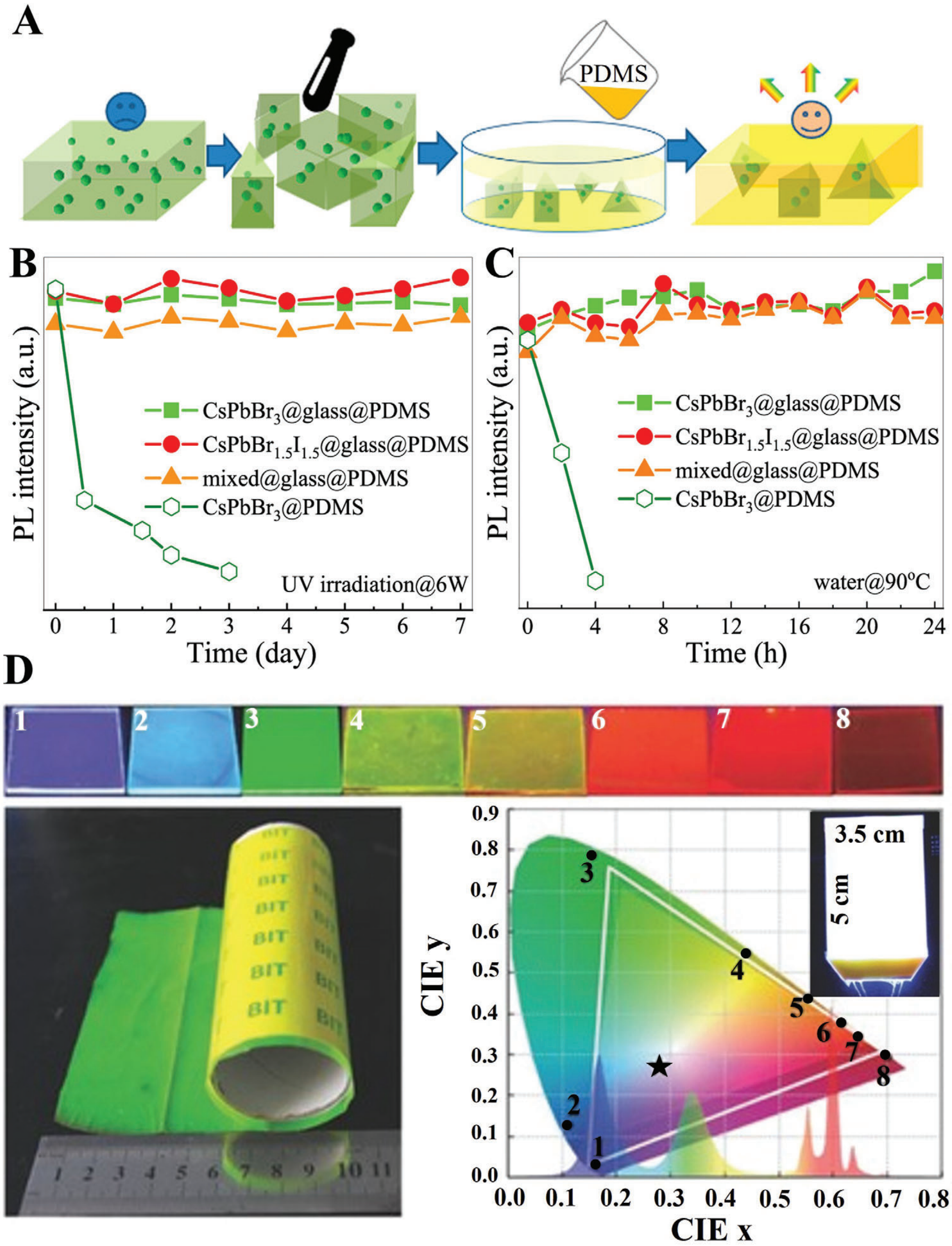

Figure 8. A) A schematic diagram of preparation of $CsPbBr_3$@Glass-PDMS composite. A low-melting glass is mixed with $CsPbBr_3$ precursor to produce $CsPbBr_3$@glass, then PDMS is used as a protective resin.[33] B) Photostability data under UV light irradiation (6 W) for 7 d. C) Humidity–resistance data under the strengthening condition by immersing $CsPbX_3$@glass@PDMS films in water at 90 °C for 24 h. As comparison, data for $CsPbBr_3$ in PDMS ($CsPbBr_3$@PDMS) are also shown in (B,C). D) Image of PVDF films with PeNCs. The color of the film can be adjusted by adjusting the perovskite precursor ratio. When this film is placed on top of the Blue BLU, in the Blue BLU/Red/Green, the blue light of the BLU is converted to light by PeNC-PVDF, to yield white light. (The red emitter was K_2SiF_6:Mn_4^+).[31] A–C) Reproduced with permission.[33] Copyright 2021, American Chemical Society. D) Reproduced with permission.[31] Copyright 2016, Wiley-VCH.

indicate that PS is packed more densely than PMMA around the PeNCs, so systems that use PS are better than systems that use PMMA.[95]

To increase the stability of PeNC in the PeNC–polymer, the penetration of H_2O into the polymer matrix must be suppressed. This goal can be accomplished by increasing the hydrophobicity of the polymer. For example, excellent hydrophobicity can be ensured by using a fluorine-containing polymer or a polymer that has many alkyl chains or aromatic rings.[59,110,111] Even if excellent hydrophobicity is secured, the miscibility between PeNCs and polymer matrix may also affect stability.

The PeNC precursor was dissolved in DMF, and the solution was directly mixed with another solution in which a polymer was dissolved in a solvent. Then the mixture was used to coat a film. Examples of polymers used in this way include PS, PMMA, polycarbonate (PC), acrylonitrile butadiene styrene (ABS), polyvinyl

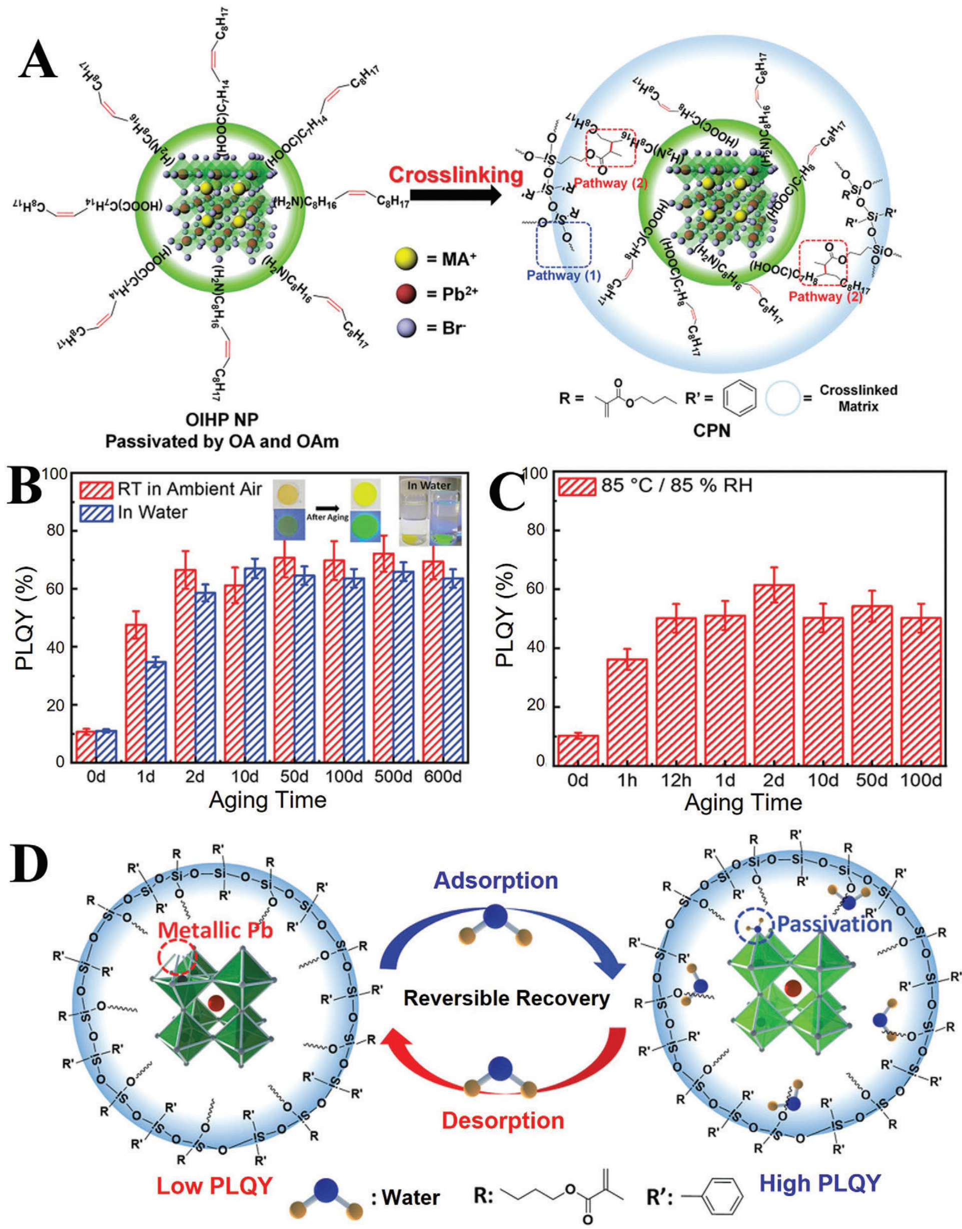

Figure 9. A) Structural diagram of the periphery of PeNCs. B) Water immersion test, and C) reliability test of PeNC film at 85 °C and 85% relative humidity. A–C) Reproduced with permission.[32] Copyright 2020, Wiley-VCH.

chloride (PVC), and cellulose acetate (CA) (**Figure 10**).[60] While the polymer dissolves in the solvent, solvent molecules penetrate interpolymer chains, so the polymer swells. When the solvent is removed after the perovskite precursor is introduced, PeNCs formed in the polymer matrix.[60] The PeNCs in PeNCs–polymer films have excellent resistance to moisture. Composite films composed of PeNCs with PS, PC, ABS, or PVC films show excellent PL properties, but perovskite-CA and PMMA films are not sufficiently stable in water-rich conditions.[60] In $MAPbBr_3$-PMMA film, PL decreases relatively quickly, because the degree of PMMA swelling in the DMF is low.[60]

Another approach is to introduce a (meth)acrylate group directly onto the surface of PeNCs and then mix them with other monomers and oligomer solutions to prepare a copolymer that contains PeNCs.[94] All-inorganic $CsPbX_3$ were prepared in the presence of excess halide, and other co-monomers were mixed to suppress the decrease in luminescence during UV curing. $CsPbX_3$ NCs were uniformly dispersed in the resulting polymer matrix.[94] The process was used to produce $CsPbX_3$ NCs with polymers by copolymerizing methacrylic-acid-capped NCs (MA-NCs) with methyl methacrylate (MMA) (PMMA-*co*-P(MA-NC), POSS-appended methacrylate monomer (MA-POSS), or both (PMMA-*co*-POSS-*co*-P(MA-NC)). The obtained PeNC–polymer composites were highly luminescent and had excellent resistance to water and chemicals due to the protection of the PeNCs by polymers that contained the (meth)acrylate group.[94] In a

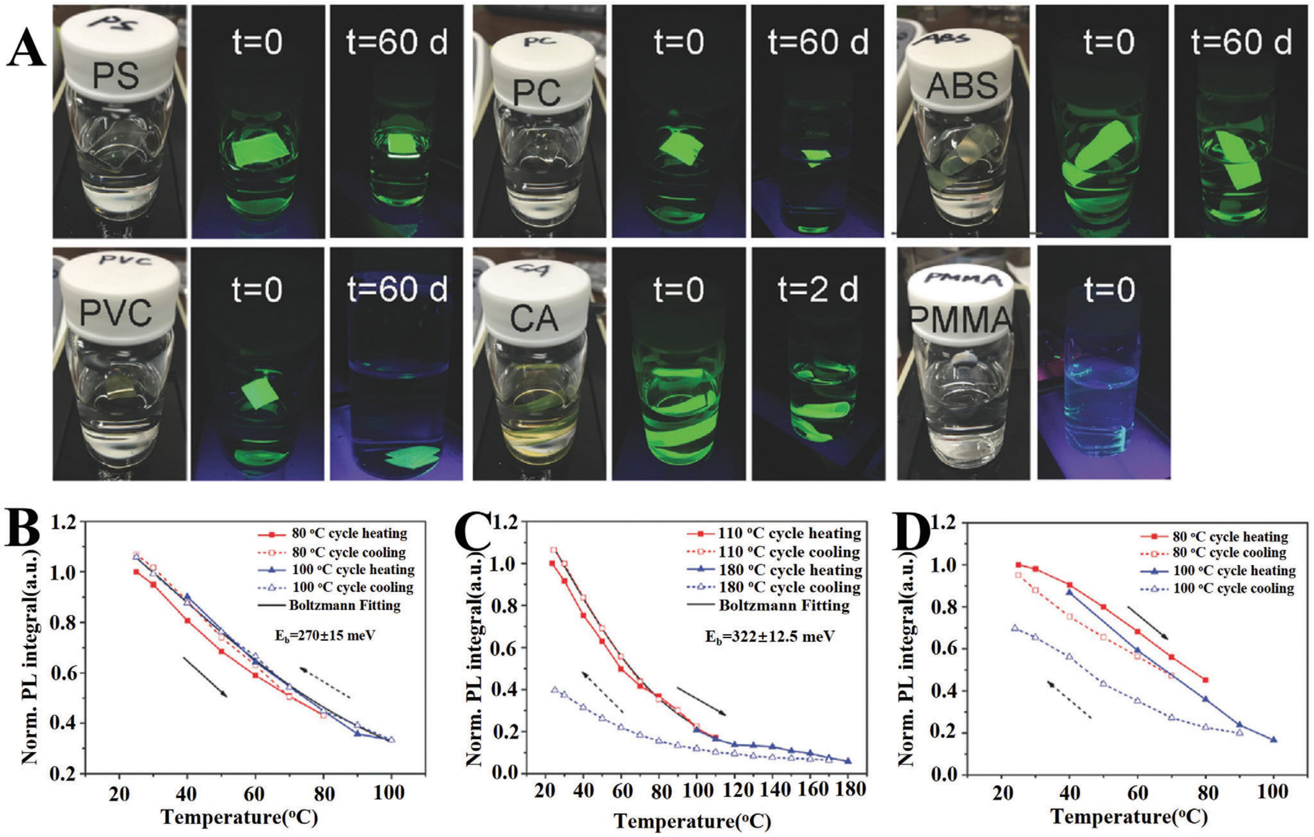

Figure 10. Water and thermal stability characterizations for various $MAPbBr_3$–polymer composite films. A) Water immersion test for various perovskite–polymer composite films. Composites of PeNCs with PS, PC, ABS, or PVC maintained PL, but composites of PeNCs with CA and PMMA lost PL in 2 d. B–D) Temperature-dependent PL of $MAPbBr_3$-PS (B), $MAPbBr_3$–PC (C), and $MAPbBr_3$–ABS (D). Squares: first thermal cycle; triangles: second thermal cycle. The solid symbols refer to heating stages and open symbols to cooling stages. Black lines in (B,C): Boltzmann fittings for reversible heating/cooling processes.[60] A–D) Reproduced with permission.[60] Copyright 2016, Wiley-VCH.

water-soaking test, PMMA-*co*-P (MA-NC) showed 49% of its initial value after 30 d, and PMMA-*co*-POSS-*co*-P (MA-NC) showed <5% of its initial value, after 60 d.[94]

As another method, presynthesized PeNC solution can be mixed with a solution in which a polymer is dissolved, then placing the mixture on a substrate, and drying the mixture to form a desired coating film.[100] The PeNCs are dispersed in a macroscale polymer, and the obtained perovskite–polymer composite has excellent luminescence, high water resistance, and good chemical resistance. Polymers used have included PS, poly(lauryl methacrylate) (PLMA), and SEBS thermoplastic elastomer; among them, PeNC-PS had the best water resistance, PeNC-PLMA had the best light resistance, and PeNC-SEBS showed the best combination of chemical resistance and light resistance.[95]

Other efforts to increase the chemical stability of PeNCs have used various polymers, including PS,[112] PMMA,[113] PDMS,[103] polyacrylonitrile,[114] poly(3,4-ethylenedioxythiophene),[115] polyvinylpyrrolidone,[116] ethylene-vinyl acetate (EVA),[117] poly(maleic anhydride-*co*-1-octadecene),[118] poly-2-vinylpyridine,[119] polystyrene-*b*-poly(ethylene oxide),[120] ethyl cellulose,[121] carboxybenzene,[122] PLMA,[95] and SEBS.[95,123]

3.5. Functional Additive Engineering

Functional materials have been mixed with PeNCs or with resins that include PeNCs. A light stabilizer, hindered amine light stabilizer (HALS) has been added to UV-curable resins to remove radicals that are generated when perovskite film is exposed to light (**Figure 11**A).[35] This method may increase the reliability of the films made of the UV-curable resins. Thermally conductive BN[36] powder modified with SiO_2 has been added to a resin that contained PeNCs that had been encapsulated with a SiO_2 layer.[51] BN dissipates heat that accumulates on PeNCs,[36] and strongly scatters light due to its high refractive index.[124]

Thermally conductive surface encapsulation of PeNCs has been achieved by forming a PeNC–SiO_2–BN composite structure (Figure 11B).[51] The structure was prepared by using SiO_2 crosslinking to intercalate $CsPbBr_3$ PeNCs within BN nanoplatelets that had been assembled layer-by-layer. The nanoplatelets are highly thermally conductive, so they provide an efficient heat-transfer path that reduces the heat accumulation on PeNCs in LEDs. Moreover, the BN–SiO_2 encapsulation resembles a ceramic and forms an excellent barrier that endows the PeNCs with high efficiency and outstanding stability under simultaneous exposure to light, air, and moisture. The PeNC–SiO_2–BN did

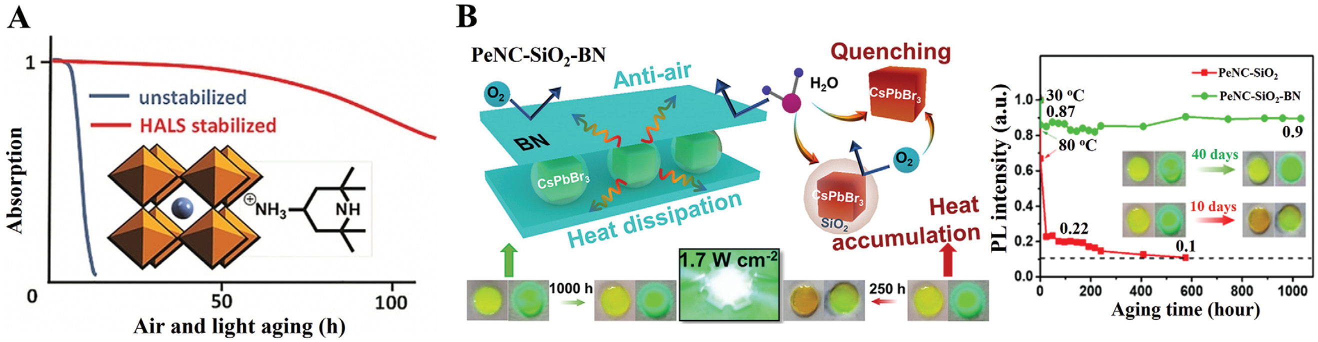

Figure 11. Examples of PeNCs stabilization using various additives. A) When HALS is added to a thin film to stabilize perovskite film, the operational stability of photovoltaics increased by more than four times.[35] B) Suppressing heat accumulation around perovskite particles and dissipating heat to the surroundings at high speed under high flux conditions caused little color change due to the minimized damage of PeNCs on the LED.[51] A) Reproduced with permission.[35] Copyright 2017, Wiley-VCH. B) Reproduced with permission.[51] Copyright 2021, American Chemical Society.

not undergo PL quenching after 1000 h of continuous illumination even under harsh conditions (405 nm blue laser at 0.31 W cm^{-2}, air with 30–40% RH, temperature = 80 °C). LEDs that used the PeNC–SiO$_2$–BN presented no light degradation after 1000 h of operation at 0.15 W cm^2 and degraded by only ≈30% at ≈1.7 W cm^{-2}. Compared with the above-mentioned study, the thermally conductive encapsulation renders the LEDs stable even at eight times higher power density while maintaining their excellent optical properties.

Mixing BN and PeNC can scatter light and dissipate heat.[36,51,124] In an experiment that used MAPbI$_3$, it degraded layer-by-layer from the surface as the temperature increased, but degradation was suppressed using *h*-BN, and a thermally stable laser with a low threshold was fabricated.[125,126] Approaches that use PVDF, glass matrix, and metal oxide (SiO$_2$, ZrO$_2$) simultaneously are the most promising candidates considering stability, simplicity, and synthetic productivity. Numerous and various approaches have been tested to improve the stability of PeNCs, with varying degrees of success (**Table 2**).

4. Film Coating

After preparing a resin including PeNCs, a film that has a desired thickness can be prepared by roll-to-roll coating.[2] When a UV-curable resin is used, a cured film is manufactured by light irradiation after slot die coating. As an initial stage for commercialization, reliability data are secured and are analyzed after film coating.

When stability against moisture of the PeNCs is not sufficiently guaranteed, two barrier coated films to protect the layer containing PeNCs can be attached to the PeNCs-containing polymer film, one on each side. Then the film has a three-layer structure: barrier film/PeNC layer/barrier film, where the barrier film is manufactured using coated barrier layer with various thicknesses and moisture permeability in accordance with a customer's request. When the barrier film is ≤50 μm thick, it can be easily damaged during further processing and so such films are not easily applied over large areas, and because of their fragility, are difficult to process, transport, and install in a display panel. When the water vapor transmission rate (WVTR) of the barrier film is too high (i.e., moisture barrier property is too low), then a barrier film cannot effectively protect the layer that contains PeNCs, and therefore may not pass the test of response to high temperature and high humidity (e.g., 60 °C/90 RH or 85 °C/85 RH); this ineffective protection impedes commercialization.

To overcome this problem, recent commercial production has mainly used barrier films that have WVTR ≈10^{-2} g m^{-2} day^{-1}. Commercial QD film vendors produce QD films that use cadmium-free QDs films for color conversion by applying two barrier films with different WVTR (one with 10^{-2} g m^{-2} day^{-1} and the other with 10^{-1} g m^{-2} day^{-1}). These barrier-film techniques can be adopted to fabricate PeNCs film for color conversion in displays.

In a QD film, the edge often becomes dark. This phenomenon is called an edge ingress and is a result damage to PeNCs by moisture and oxygen diffusing from the air into the cured polymer layer through the surface or edge of the film. Damage to the surface PeNCs decreases their luminescence, so the damaged film turns transparent or dark. To solve the edge ingress problem, strategies have been developed to prevent direct contact between the air and the PeNC layer by attaching barrier films to the surface of the PeNC layer to suppress inward diffusion of air and moisture, or by introducing predesigned patterns in the UV layer to minimize H$_2$O diffusion into the UV layer and to act as a guide to the film thickness.[139]

4.1. Measuring of the Stability of Downconversion Films

After the film is manufactured, its reliability should be checked prior to commercialization to verify that the film can be used in an actual display module (e.g., LCD). To be suitable for commercialization, the film must surpass the specified specifications, such as those in **Table 3** for commercial QD films for downconversion-type LCD TVs, which are currently commercially produced. Room temperature storage test, high temperature module operation test, high temperature storage test, high temperature and high humidity test, thermal shock test, and cold resistance test are performed. The basics are similar to the specifications presented here, but specification can be adjusted loosely or tightly upon request of film customers. Nanometer-sized PeNCs have a large specific surface area and are particularly sensitive to heat, light, and moisture, so data for these are collected by focusing on high-temperature storage tests

Table 2. PeNCs stability under light, heat, and moisture.

PeNCs	Synthesis method	Test condition	Stability[a)]	Ref.
$CsPbBr_3$-$ZnBr_2$	Hot injection/post treatment	RH[b)] 60%	6 d, 0.60	[14]
$CsPbBr_3$	Hot injection	RH 60%	6 d, 0.20	[14]
$CsPbBr_3$	Hot injection	Thermal cycling (20–100 °C)	≈0.6	[19]
Al^{3+}-$CsPbBr_3$	Hot injection/doping	Thermal recycling (20–100 °C)	≈0.95	[19]
$CsPbX_3$-DDT[c)]-AlX_3	Hot injection/post treatment	Storage stability	16 d, 0.80–0.90	[20]
$CsPbCl_3$-YCl_3	Hot injection/post treatment	Ambient storage	14 d, ≈1.0	[21]
$CsPbI_3/Cs_4PbI_6$	Hot injection/core–shell	Ambient storage	7 d, 0.525	[78]
$CsPbI_3$	Hot injection	Ambient storage	2 d, 0	[78]
$CsPbBr_3/Rb_4PbBr_6$	Hot injection/core–shell	450 nm, 175 mW cm^{-2}	46 h, 0.83	[46]
$CsPbBr_3/Cs_4Pb_2Br_5$-PMMA	Mechanical grinding/polymer encapsulation	Water stability	40 d, 0.80	[79]
$CsPbBr_3$/ZnS	Hot injection/core–shell	Water stability 50 mW LED	48 h, 0.50 48 h, 0.80	[47]
$CsPbI_3$/PbS	Hot injection/core–shell	Ambient storage	35 d, 0.97	[80]
$CsPbBr_3$/CdS	Hot injection/core–shell	RH 75% 60 °C	13.5 h, 0.83 9 h, 0.40	[81]
$CsPbBr_3$-SBE[d)]	Hot injection	Ambient storage	28 d, 0.80	[27]
AHDA[e)]-$CsPbI_3$	Hot injection	Ambient storage	110 d, 0.99	[28]
$CsPbBr_3$	Drop casting precursor solution (bulk sample fabrication)	RH 60–70% Solar simulated light 6 h	Unchanged Unchanged	[85]
OPA[f)]-$CsPbBr_3$	Hot injection	RH 50%/25 °C	3 d, 0.90	[91]
$CsPbI_3$-DDT	Hot injection	RH 73%/365 nm UV	3~4 d, 0.90	[92]
$CsPbBr_3$-V18[g)]	LARP	Ambient storage	30 d, ≈1.0	[48]
$CsPbBr_3$-CLA[h)]	Hot injection	Water stability	3 h, 0.7	[127]
Mesoporous SiO_2-$CsPbBr_3$	Hot injection	UV light (365 nm, 6 W)	96 h, 0.80	[49]
$CsPbBr_3$	Hot injection	UV light (365 nm, 6 W)	96 h, 0.40	[49]
$CsPbBr_3$–SiO_2	Hot injection	Ambient storage	3 month, 0.95	[30]
$CsPbX_3$/Oxide	Hot injection	375 nm LED 117 mW cm^{-2}/40 °C	10 h, 0.98	[101]
$CsPbX_3$/AlOx	Hot injection-ALD[i)]	365 nm UV 100 mW cm^{-2}	8 h, 0.90	[34]
$CsPb(Br_{0.35}I_{0.35})/CsPb_2Br_5$ $CsPbBr_3/CsPb_2Br_5$	Hot injection/core–shell	UV Water stability RH 33%/100 °C UV Water stability RH 33%/100 °C	10 d, 0.93 10 d, 0.94 24 h, 0.42 10 d, 0.90 10 d, 0.88 24 h, 0.25	[105]
$CsPbBr_3$@glass@PDMS	Melt quenching/precursor glass form	6 W UV light Water, 90 °C	7 d, 1.0 24 h, 1.0	[33]
$MAPbBr_3$-PDMS-urea gel	LARP	Water stability	9 d, 0.67	[128]
$MAPbX_3$-PVDF	In situ fabrication $MAPbBr_3$-PVDF	6 W 365 nm UV RH 85%/70 °C	400 h, 0.92 216 h, ≈ 0.0	[31]
$MAPbBr_3$-siloxane	LARP	RH 85%/85 °C	100 d, >5.0	[32]
$MAPbBr_3$-PS $MAPbBr_3$-PC		100 °C 110 °C 140 °C 180 °C	300 h, 0.7 ≈1.2 ≈1.4 <50 h, 0.25	[60]
$CsPbBr_3$-PMPOPNC	Hot injection	Water stability UV	100 d, >0.80 144 h, ≈ 0.90	[94]
$CsPbBr_3$-PLMA,SEBS,PS	Hot injection	Water stability	125 d, 1.0	[95]
$CsPbBr_3$/PMMA	Microfluidic-spinning microreactor	RH 70%/30 °C	3 d, 0.75	[113]

(Continued)

Table 2. (Continued).

PeNCs	Synthesis method	Test condition	Stability[a)]	Ref.
$MAPbBr_3$-PFN[j)]	Electrospinning process	RH 80%/28 °C Water stability	>25 d, 1.0 48 h, ≈ 0.5	[114]
$CsPbBr_3$-EVA	LARP	Ambient storage	200 h, 1.0	[117]
$CsPbBr_3$-poly maleic anhydride[k)]	Hot injection	100 mW UV-LED	12 h, 0.70	[118]
PEO-*b*-PS[l)] grafted $MAPbBr_3$	LARP	365 nm UV light 7.0 mW cm^{-2}	100 min, >0.80	[120]
$CsPbBr_3$-ethyl cellulose	Hot injection	Ambient storage	150 h, >0.87	[121]
$CsPbBrX_3$-plasma		Storage stability 6 W 365 nm UV lamp	11 d, 0.90 8 h, 0.95	[129]
$MAPbBr_3$	Ultra-sonication (Top-down)	6 W UV lamp	120 min, 0.85	[130]
$MAPbBr_3$	LARP	6 W UV lamp	120 min	[130]
$CsPbBr_3$	Hot injection	6 W UV lamp		[130]
$MAPbBr_3$–SiO_2	LARP	470 nm LED	7 h, 0.90	[131]
$MAPbBr_3$	LARP	470 nm LED	7 h, <0.4	[131]
$CsPbBr_3$-K-oleate	Hot injection	RH 60%/50 °C	30 h, 0.979	[132]
$CsPbBr_3$	Hot injection	RH 60%/50 °C	30 h, 0.163	[132]
$CsPbBr_3$-S^{2-}	Hot injection	175 mW 450 nm LED	42 h, 0.04	[133]
$CsPbBr_3$-S-In	Hot injection	175 mW 450 nm LED	188 h, >1.0	[133]
$CsPbBr_3$	Hot injection	175 mW 450 nm LED	7.67 h, almost 0	[133]
$CsPbBr_3$-DBSA[m)]	Hot injection	405 nm 820 mW cm^{-2} laser flux	400 min, 0.68	[26]
$CsPbBr_3$-paraffin	Ultra-sonication	365 nm UV light	3000 s, 0.86	[134]
$CsPbBr_3$-paraffin	RT supersaturated recrystallization	365 nm UV light	3000 s, 0.57	[134]
$CsPbBr_3$	Aqueous phase exfoliation	365 nm UV light	2 h, 0.85	[135]
$CsPbBr_3$	Hot injection/DEZ[n)] injection (Fusion process)	UV light	60 min, 0.93	[136]
$CsPbBr_3$	Hot injection	UV light	60 min, 0.085	[136]
$CsPbBr_3$-L-type ligand[o)]	LARP	UV light	1 h, 0.80	[38]
$CsPbBr_3$-NBS[p)]	Hot injection	365 nm, 8 W UV light	24 h, 0.80	[137]
Ni-doped $CsPbBr_3$	Hot injection	365 nm, 4 W UV light	48 h, 0.82	[72]
$CsPbBr_3$	Hot injection	365 nm, 4 W UV light	48 h, <0.3	[72]
Mg-doped $CsPbBr_3$	Hot injection	365 nm 8 W UV light	38 h, 1.0	[73]
$CsPbBr_3$/$FSiO_2$/PDMS	Hot injection	RH 60%/25 °C	90 d, 0.965	[111]
$CsPbCl_3$	Hot injection/anion exchange	150 W Xenon lamp	24 h, 0.80	[138]
Yb^{3+}-doped $CsPbCl_3$	Hot injection	60 W 365 nm UV lamp	85 h, 0.20	[71]

[a)] Relative to initial value (I/I_0); [b)] Relative humidity; [c)] 1-dodecanethiol; [d)] 3-(*N*,*N*-dimethyloctadecylammonio)-propanesulfonate; [e)] *N*′-(2-aminoethyl)-*N*′-hexadecylethane-1,2-diamine; [f)] Octylphosphonic acid; [g)] 4-vinylbenzyl-dimethyloctadecylammonium chloride; [h)] Conjugated linoleic acid; [i)] Atomic layer deposition; [j)] Poly[(9,9-bis(3′-(*N*,*N*-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)]; [k)] Poly(maleic anhydride-*alt*-1-octadecene); [l)] Polystyrene-*b*-poly(ethyl oxide); [m)] Dodecylbenzene sulfonic acid; [n)] Diethylzinc; [o)] Primary amine for L-type ligand; [p)] *N*-bromosuccinimide.

Table 3. Reliability test condition and specifications for downconversion-type LCD TV panels (e.g., commercialized QLED TV).

No.	Test item	Test condition	Specification (Requirements)	Comment
1	High-temperature storage	60 °C	500 h PASS[a)] 1000 h PASS[b)]	
2	Low-temperature storage	−30 °C	500 h PASS[a)] 1000 h PASS[b)]	
3	High temperature, High humidity	60 °C, 90% RH	500 h PASS[a)] 1000 h PASS[b)]	
4	Temperature cycle	Temperature cycling from −30 to 70 °C	500 h PASS[a)] 1000 h PASS[b)]	4 h $cycle^{-1}$
5	High-temperature operation	60 °C	500 h PASS[a)] 1000 h PASS[b)]	Commercially available downconversion-type LCD panel

[a)] PL intensity <5% decrease, color change <0.5%; [b)] PL intensity <10% decrease, color change <1%, edge ingress ≤1 mm.

and high-temperature operation tests. The specifications of all tests depend on the time to proceed with reliability. For commercialization, after 500 h operation, PL intensity decrease should be <5% and the color change (Δx, Δy) should be <0.5%. At 1000 h operation, the luminance decrease should be <10%, and the color change (Δx, Δy) should be <1%, and the depth of edge ingress should be <1 mm (Table 3). The reliability of QD film is determined to be satisfactory only when requirements for 500 and 1000 h operation are all satisfied.

5. Downconversion Perovskite Displays

5.1. Large-Sized LCD TV with PeNCs

Due to the intrinsic instability of PeNCs, downconversion films that use them usually have a three-layer structure with a barrier film on both sides of a PeNC layer. Commercial barrier films have been developed to prevent penetration of H_2O and O_2, and their main purpose is to protect PeNCs from them.[140]

To verify the concept of downconversion films that use PeNC, green-emitting PeNC polymer films in nonreactive PS or PMMA and red-emitting polymer films that use CdSe QDs were manufactured on glass substrates and assembled to form a downconversion layer for an LCD panel.[60] Overall, the assembled downconversion system covered 95% of the Rec. 2020 color area and >100% of the Adobe RGB color area.[60]

Quantum Solutions Co. Ltd. reported harsh acceleration tests by monitoring PLQY for samples irradiated with a blue-light LED at 10 W m^{-2} power for 1000 h. PLQY and full-width at half-maximum (FWHM) did not change during this test. This result shows that PeNCs have the potential to be commercialized. The proposed LCD had on-surface structure where a downconversion film, which also acts as a light diffusing film, is located on the surface of light guide panel[2] and used hybrid emitters which is the mixture of PeNCs and QDs for green and red emission. In the absence of a hybrid mixing method, the exchange of Br$^-$ from green-emitting PeNCs and I$^-$ from red-emitting PeNCs cannot be prohibited when two types of perovskite particles are dispersed in the same resin, giving lower color gamut than expected. However, to obtain an inexpensive display, the simplest and cheapest process is to use only one type of particles in the display.[61,62]

Researchers have manufactured PeNC films by using an ex situ method to synthesize and disperse PeNCs in various polymer matrices.[60–62] Meanwhile, a PeNC film was prepared by in situ crystallization, e.g., green-emitting PeNCs were synthesized by an in situ method that uses PVDF and a PeNC precursors in a DMF solution during a swelling–deswelling process. The PeNC film was applied to blue LEDs with a red light-emitting phosphor, K_2SiF_6:Mn_4^+ (KSF) to achieve white light emission, then applied to prototype LCD TVs.[58]

Patents have been granted for numerous processes to produce PeNCs and devices that use them (**Table 4**). SN Display Co. Ltd. in Korea holds the original patents that have been originally claimed in 2014 for PeNC materials, PeNC thin-film process, downconversion films and displays, and PeNC EL devices.[141–147] SN Display is developing technologies to future self-emissive displays which can be employed to specialized display products and AR/VR displays. PEROLED holds patents for synthesis of PeNC materials, PeNC encapsulation, and PeNC downconversion films for small/medium size displays and AR/VR displays. Avantama holds patents for encapsulation to form protective films on the surface of the luminescence,[148,149] and manufactures and sells hole-transport layer and electron-transport layer materials for EL application of PeNCs. Nanolumi is selling perovskite color-conversion film under the CHAMELEON GFILM trademark with technical support from the National University of Singapore. Nanolumi holds patents for continuous synthesis process and is selling a color-conversion film that has high flux stability at 100 mW cm^{-2} and undergoes minimal color change during a 1000 h reliability test. Helio Display focuses on developing downconversion films for downconversion displays. Recently, a research team at Seoul National University has demonstrated displays composed of a downconversion film with green $MAPbBr_3$ PeNCs (FWHM ≈20 nm) and red CdSe/ZnS core–shell QD (FWHM ≈30 nm) on a blue backlight with a 10.1 in. LCD (**Figure 12**A) and a 28 in. LCD at CES (Consumer Electronics Show) 2020 in collaboration with PEROLED Co. Ltd. (Figure 12B).

5.2. AR/VR Approaches

AR and VR devices are being developed as next-generation display platforms to increase the realism of human-digital interactions.[150] Near-eye displays for VR/AR applications require high-resolution pixels (>2000 PPI) to provide high-quality images. High absorption coefficient and near-100% PLQY endow lead halide PeNCs with high color-conversion efficiency, so in theory, the of PeNC color-conversion layer can be very thin (<6 µm). This feature facilitates fabrication of very fine pixels for high-resolution displays in small area. Various techniques have been applied to produce high-resolution (e.g., pixel sizes smaller than 10 µm) perovskite patterns. Examples are X-ray/electron beam lithography,[129,151] laser direct writing,[152] micro- and nanoprinting techniques,[153] and photolithography.[154,155] However, the research on the integration of patterns and devices has been rarely reported.

3D direct lithography of PeNCs with tunable bandgap and composition in glass has been demonstrated.[156] The resulting glass-encapsulated PeNCs had excellent stability against UV irradiation, organic solvents, and temperatures up to 250 °C. This lithographic technique can enable one-step fabrication of multicolored PeNC patterns that have dot size <10 µm and that can be integrated with a holographic display device. A dynamic holographic display was realized by switching among holograms and was used to realize a 3D holographic display that used these PeNC patterns.[156] Holographic images could be reconstructed simultaneously in multiple planes along the light propagation direction.

6. Conclusion and Perspective

This review has introduced the basic structure, synthesis methods, and surface properties of PeNCs, and then material engineering when PeNCs are used in color-conversion films. We systematically summarized recent progress on stability improvement of PeNCs for light downconversion displays, by exploiting: 1) defect engineering, 2) use of core–shell heterostructures,

Table 4. Vendors for PeNCs and related commercial products.

Vendor (Headquarter)	Summary[a)]
SN Display (South Korea)	– Commercialization: PeNCs and electroluminescence (EL) devices. – Patent: Materials of PeNCs, process of PeNC thin film, light-converting film and display, EL devices/solar cells. – Interest: Patent license, EL display, AR/VR applications, X-ray detectors.
PEROLED (South Korea)	– Commercialization: PeNCs, color ink, downconversion films and color-filters – Patent: Synthesis, encapsulation, light-converting film – Interest: Light-converting film (with ultra-stability) – 28" Downconversion-type LCD Monitor demo at CES2020 (Collaboration with Seoul National University, Prof. Tae-Woo Lee' group)[2] – home page: http://www.peroled.co.kr/
Avantama (Switzerland)	– Commercialization: PeNCs and optoelectronic materials. – Patent: Perovskite synthesis, encapsulation, and light converting film – Interest: Light-converting application – home page: https://www.avantama.com
Quantum solutions (Saudi Arabia)	– Commercialization: PbS QDs, PeNCs – Patent: CsPbBr3 continuous synthesis, light converting film – Interest: Light-converting application – home page: https://www.quantum-solutions.com/
Nanolumi (Singapore)	– Commercialization: PeNCs, light-converting film (Chameleon(R) G Film) – Patent: Continuous synthesis – Interest: Light-converting application – home page: https://www.nanolumi.com/
Helio Display Materials (England)	– Commercialization: Downconversion films and color filters – Patent: Not found yet. – Interest: Perovskite color-filter – home page: https://www.heliodisplaymaterials.com
Zhijing Nanotech (China)	– Commercialization: Downconversion films – Patent: LARP synthesis, in situ film formation – Interest: Light-converting film (in situ film formation) – Collaboration with TCL for downconversion type 75" LCD TV (500 set production) – home page: http://www.zhijingtech.cn/

[a)] Data from homepage of each vendor.

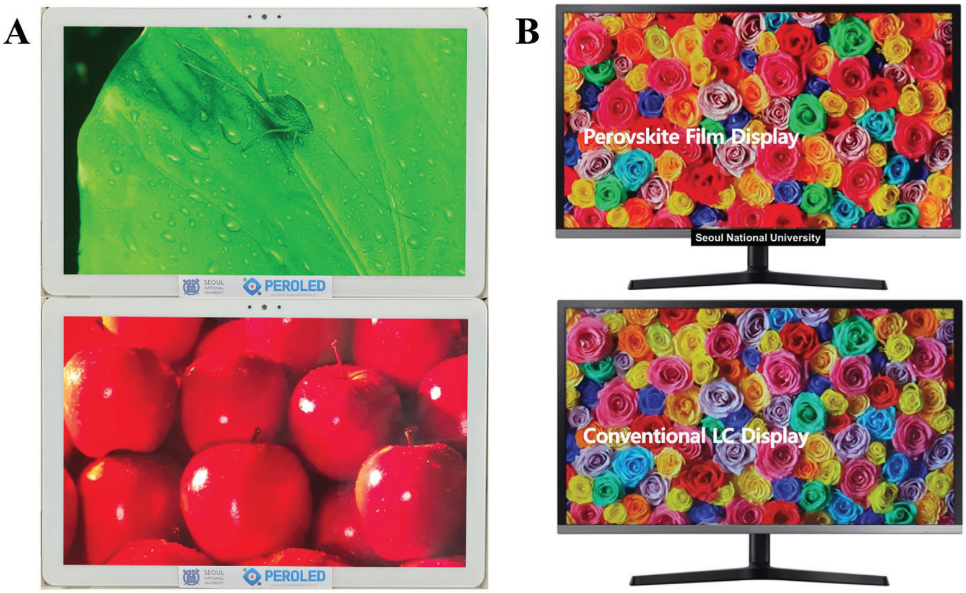

Figure 12. Example of PeNCs applications in display. A) Green and red image demonstration of a tablet comprising PeNC downconversion film with green $MAPbBr_3$ PeNCs (FWHM ≈20 nm) and red CdSe/ZnS core–shell QD (FWHM ≈30 nm) on a blue backlight in an LC display 10.1 in. tablet. B) 28 in. perovskite film display versus 28 in. conventional LC display. B) Reproduced with permission.[2] Copyright 2020, Wiley-VCH.

3) ligand engineering, 4) encapsulation engineering, and 5) functional additive engineering. We followed by introduction of the methods to coat PeNC film and standard conditions to test the reliability of downconversion films to assess their compatibility with commercialization. Motivated by the advantages of PeNCs and significantly improved stability, several start-up companies (SN Display (Korea), PEROLED (Korea), Avantama (Switzerland), Quantum solutions (Saudi Arabia), Nanolumi (Singapore), Helio Display Materials (England), Zhijing Nanotech (China)) have shown the TV and monitor demonstrations based on PeNC film-LCD backlights. All these advances indicate the great potential of PeNC emitters for the next-generation vivid and high-resolution displays.

Although the great progress has been achieved, there are a few key challenges and application directions to be further explored. Current commercial light-conversion films have focused on green-emitting PeNCs, which are combined with red-emitting CdSe QDs, InP QDs, or KSF for LCDs, but to realize displays that have high color purity and wide color gamut, a 100% PeNC film must be developed. This goal is impeded by two main obstacles: 1) diffusion of mobile ions between red-emitting PeNCs and green-emitting PeNCs; 2) poor stability of red-emitting PeNCs that satisfy REC. 2020 color gamut. Therefore, new stabilization strategies must be developed to precisely encapsulate PeNCs at a single-particle level. In addition, pure red light is emitted from either mixed-halide or quantum-confined perovskite nanostructures; this arrangement imposes two challenges: to suppress light-induced phase separation from the mixed halides and to stabilize small ionic NCs for the quantum-confined nanostructures. Possible methods to solve the instability problems of red-emitting PeNCs include developing robust-binding ligands, engineering the composition of the A-site, and selecting appropriate encapsulation methods.

Although downconversion-type LCD TVs that use a QD enhancement film are currently commercialized, the reduction of their thickness is constrained, and they are expensive due to use of a huge number of QDs. Accordingly, research and development on QD-OLED and QD-EL are underway, but only QD-OLEDs has been commercialized; the other technologies are under development. Therefore, as new types of displays for AR and VR emerge, they will require high absorption coefficients in thin films that have narrow pixels and low power consumption; PeNCs can meet these requirements, so demand for PeNCs will increase. Particularly, PeNCs will have niche applications such as small- and medium-sized displays and AR/VR displays in which conventional QDs are difficult to apply because of the requirement of high resolution in small area. Efforts have been made to reduce the thickness and cost of displays. Samsung Electronics of Korea commercialized QD-OLED technology in November 2021, and is moving toward QD-EL. Although this trend lowers the overall proportion of QD enhancement film markets, the demand for low-cost narrow-band emitters with high absorption coefficient for pixelated color conversion in high-resolution displays is still increasing. Use of PeNCs has the potential to meet this demand.

PeNCs with high color purity and high color conversion efficiency also have potential applications in vivid and high-resolution VR/AR displays. However, current research on the patterning of lead halide PeNCs and their integration with VR/AR devices is still in the preliminary stage. Current patterning methods generally damage PeNCs and weaken their luminescence because of their labile crystal structure and poor encapsulation. Therefore, nondestructive patterning methods should be developed. Pre-encapsulation of each PeNC individually may help to retain its structural and optical properties during the patterning process. In addition, a few prototypes of perovskite micro-LEDs under current driving have been demonstrated recently; they provide an alternative approach to development of near-eye VR displays.[157,158] In this technology, fabrication of stably electroluminescent devices requires development of methods that prevent electrically induced ion migration; use of epitaxial metal chalcogenide shells on PeNCs may be a way to solve this problem.[46,47]

The solution-processed property of PeNCs makes them compatible with use in flexible and stretchable displays. Recently, a flexible and stretchable light converting layer has been fabricated using PeNCs and SEBS polymers.[65] It operates normally even when stretched 100%, and light conversion is performed using a blue LED. Future work should focus on increasing the brightness and operational stability of stretched PeNC films. Strategies to perfectly surface-passivate and covalently link PeNCs to a stretched polymer may enable fabrication of efficient and stable stretchable displays.

Finally, the toxicity of the lead in these perovskite emitters cannot be ignored. Although no nation currently bans the sale of displays that contain lead, some communities (i.e., the EU) limit the content of lead in the final product. Therefore, lead-reduced or lead-free perovskite emitters must be developed. Recently, a SnF_2-derived Cs_4SnBr_6 PeNCs showed a high PLQY of 62.8%, and excellent stability against oxygen, moisture, and light radiation for 1200 h.[159] However, the currently available lead-free perovskite emitters generally have broad-band emission and are therefore suitable only for white-light illumination. Therefore, B-site ionic doping to reduce lead content and perfect encapsulations of PeNCs to avoid leakage of lead are more promising pathways than use of Sn perovskites, toward safe and ecologically benign displays.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

AR/VR display, down-conversion, perovskite nanocrystals, QLED displays, quantum dots

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