Emerging Solution-Processable Luminescent Nanomaterials in Hybrid Structures Offer New Solutions for Displays and Lighting

As the development of quantum dot and perovskite luminescent materials accelerates, it is expected that these materials will increasingly gain applications in display and lighting markets, particularly in hybrid structures with state-of-the-art phosphor or OLED systems.

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Solution-processable semiconducting nanomaterials, including cadmium-based or cadmium-free colloidal quantum dots (QDs)1,2 and, most recently, metal-halide perovskites3, have emerged from academic labs to become promising luminescent component materials for optics and optoelectronics in the display and lighting industries. Working as independent players in either photoluminescence (PL) or electroluminescence (EL) mode, these materials could help two competing display technologies (LCDs and organic light-emitting diodes [OLEDs]) in achieving better color quality and higher efficiencies. A recent article published in this magazine by Wang and Sun,4 “Quantum-Dot and Quantum-Rod Displays – the Next Big Wave,” provided a comprehensive overview of this technology, covering both QD-enhanced LCD products in the market and active QD LED research in the lab.

QDs and perovskites are often touted as disruptive material systems that could completely replace traditional phosphor-based LEDs for backlighting LCDs or organic material-based OLEDs. In the near future, however, these materials are more likely to complement than to replace traditional technologies for optimizing color and efficiency in display and lighting applications.

This article will provide an overview of the technology status of solution-processable luminescent QDs and metal-halide perovskite nanomaterials, as well as a report on some of the most recent developments on both PL and EL fronts, and a vision of how these materials could work with traditional technologies in hybrid structures for display and lightings in the near future.

Status Overview of Colloidal Quantum Dots and Perovskites: Merits and Challenges

As outlined in Wang and Sun’s article4, the merits of QDs and perovskites include:

• Precisely tunable emission wavelength through size and/or composition control of QDs and perovskites that can cover a wide range of wavelengths (Fig. 1)
• Highly saturated colors (narrow emission bandwidth)
• High luminescence efficiency
• The ability to be easily solution-processed into large areas with thin, flexible form factors

Fig. 1: The tunable emission spectral range of solution-processable colloidal quantum dots is shown at the top and that of perovskite materials is shown at the bottom.
A closer look at these specific material systems can provide a better understanding of their merits and respective remaining challenges.

**Colloidal Quantum Dots: Cd-based vs. Cd-free**

Colloidal QDs are nanometer-sized (e.g. 2 ~10 nm) semiconductor particles whose optical properties are mainly determined by the so-called quantum confinement effect. Simply put, the quantum confinement effect indicates that when the sizes of the semiconductor nanoparticles fall below a certain value, their effective electronic and optical properties (and hence the fluorescent light wavelength) will deviate from the value of their bulk counterpart and be dependent on the particle size. The smaller their size, the larger their electronic bandgap (and thus the shorter their emission wavelength) will be. Therefore, the emission wavelength of QDs can be tuned simply by adjusting the particle size during the synthesis process. The purity of the emission color will depend on the size distribution of the nanoparticles.

As the most developed and well-characterized QD material system, II-VI semiconductor cadmium selenide (CdSe) has a bulk bandgap value of 1.73 eV (corresponding emission is ~716 nm). As schematically illustrated in Fig. 1, the emission spectrum of CdSe-based QDs can be adjusted to cover the entire visible region by tailoring their particle size. State-of-the-art CdSe-based QDs exhibit a quite narrow full width at half maximum (FWHM) of 20 ~ 30 nm and super-high luminous quantum efficiency (> 95%). QD materials with such high optical quality seem to be a perfect choice for display applications and have already been employed in some commercial products since the first generation QD-enhanced LCD TV (with QD components from QD Vision) was released by Sony in 2013, followed by other brands such as TCL, Haisen, etc. However, cadmium is considered a toxic element, and the Restriction of Hazardous Substances (RoHS) directive issued by the European Union requires that the maximum cadmium content be less than 100 parts per million (ppm) in consumer electronic products. This has been a major concern and has limited the industry’s adoption of CdSe-based QDs.

The other established QD system, indium phosphide (InP), which is cadmium-free, has a smaller bulk bandgap value of 1.35 eV (corresponding emission ~918 nm). As a result, to reach the same emission wavelength, the size of InP QD particles has to be much smaller than that of CdSe QDs (Fig. 1). This restriction complicates the nanocrystal synthesis process and makes InP QDs’ size distribution difficult to control. Thus, the emission of InP-based QDs generally has a broader FWHM (> 40 nm) and lower efficiency. Despite the existing performance gap, InP-based QDs have gained significant momentum, as exemplified by Samsung’s recent flagship SUHD TVs, which have been rebranded as QLED TVs for 2017. It should be noted that Samsung’s “QLED” TVs remain PL-based LCD products and shouldn’t be confused with the emissive EL QLEDs to be discussed later on.

**Metal Halide Perovskites: History and Challenges**

Metal halide perovskites are a group of emerging optoelectronic materials with perovskite structure AMX₃, where X is generally a halide (F, Cl, Br, I) anion, and M and A are cations of different sizes. The smaller cation M is usually a divalent metal (Pb²⁺, Sn²⁺, or other metal ions) with stable octahedral coordination, forming an extended network of MX₆ octahedra intercalated with larger organic or inorganic cations of A (Fig. 2). Among the many options of A cations, of particular interest to the display community could be the organic methylammonium (CH₃NH₃⁺, MA) or cesium (Cs⁺) ions, since compounds of these two (e.g. MAPbX₃ or CsPbX₃) exhibit optical properties of similar or even better performances than QDs for certain colors (e.g. green).

While the recent fame of perovskite materials is mainly due to the unprecedented efficiency gains of organic-inorganic perovskite (OIP) based solar photovoltaics, the history of perovskite research for displays can be traced at least as far back as the 1990s, when David Mitzi at IBM systematically studied OIPs for light-emitting devices and thin-film transistors. Recently studies on metal halide perovskites have extended the materials systems to include both OIPs (e.g. MAPbX₃ (X=Cl, Br, I)) and purely inorganic perovskites such as CsPbX₃ (X=Cl, Br, I) (Fig. 1). Meanwhile, the merits of most perovskites seem to resonate with those early considerations of OIPs in the 1990s: (i) these materials can be easily solution-processed into crystalline thin films; (ii) with simple tuning of the halide components, they can emit over the entire visible spectrum; (iii) the purity of their emission color seems to be relatively independent of their particle size. Particularly for CH₃NH₃PbBr₃ or CsPbBr₃, highly efficient green emission with a narrow FWHM of less than 20 nm can be achieved even with large particle size variations. This capability makes these perovskites especially promising for wide-color-gamut display applications.

It should be noted that the original challenge that hindered Dr. Mitzi from further exploration of OIPs is still relevant today. Most perovskite materials have major stability issues. The instabilities of perovskites are often attributed to their low formation energy, or the energy needed to form them (~0.1–0.3 eV), which makes it easy for them to be...
veniently solution processed, but also renders them vulnerable to external stresses, such as moisture, heat, light, or electrical field.\textsuperscript{8,10} It has been observed that, in the presence of moisture and oxygen, the OIP grains grow spontaneously even at room temperature, leading to a higher density of defects and a shorter carrier lifetime.\textsuperscript{11} While it can be envisioned that OLED encapsulation technology such as cover glass or barrier films could help protect perovskite devices as well, the intrinsic stability of perovskite materials also needs to be significantly enhanced.

Three passivation strategies have been developed to stabilize perovskites, with successes of different levels. One commonly used approach involves film formation through impregnation and pore filling of a pre-formed mesoporous inorganic matrix (such as TiO\textsubscript{2} or Al\textsubscript{2}O\textsubscript{3}) with the perovskite precursor solutions.\textsuperscript{3,7} However, the solvent evaporation from pre-formed, and thus static, inorganic porous structures will inevitably lead to partially exposed, unprotected perovskites. In fact, it has been reported that significant decomposition already occurs during annealing of perovskites on porous TiO\textsubscript{2} at 85°C, even in an inert atmosphere. Further coverage of these perovskite films with carbon nano-tube/polymer composites demonstrated impressive “water-resistant” devices, but such macroscale passivation leaves perovskites vulnerable to potential degradation due to film leakage.

The second strategy, solution-based synthesis of surfactant-protected perovskite nanoparticles, employs a surfactant-assisted growth technique similar to Cd-based QD synthesis. This technique can achieve passivation of individual nanocrystal grains and lead to colloidal perovskite QDs (both OIPs\textsuperscript{12–15} and inorganic perovskites\textsuperscript{16,17}) with enhanced stability and photoluminescence quantum yield (PLQY). As shown in Fig. 3, by tuning halogen components, the emission spectra of both MAPbX\textsubscript{3} and CsPbX\textsubscript{3} QDs can cover the entire visible spectrum. Of the various demonstrated colors, the green emission of bromide perovskites (MAPbBr\textsubscript{3} and CsPbBr\textsubscript{3}) stands out with its ultra-high color purity (FWHM <20 nm) and high PLQY (~70–90%). This green purity is particularly interesting for display applications, because the human visual system is very sensitive to green color, and slight changes in green can lead to big color gamut variation. By comparison, even the best CdSe-based green QDs normally show a broader emission, with FWHM > 25 nm. While surfactant passivation can stabilize perovskite QDs in the solution phase, when they are processed as thin films, their efficiency tends to be substantially reduced because of quenching induced by spontaneous QD aggregations.\textsuperscript{18} In addition, the reaction yield of perovskite QDs remains low. The large overlap between absorption and emission spectra [Fig. 3(e)] also indicates that self-absorption could be an issue for PL or EL applications.

The third strategy involves deposition of composite films from mixtures of perovskite precursors with protecting media, such as organic small molecules, polymers,\textsuperscript{19} or inorganic nanoparticles.\textsuperscript{20} Although inherently simple, this approach often results in serious phase separation between OIPs and the protecting media, leading to large OIP grain-size variation, broad PL peaks, lower PLQY, and unsatisfactory robustness. In the most recent study, by controlling the crystallization process from precursor solutions, a green perovskite containing polymer films with very high PLQY (94%) was reported, although its thermal stability remains unsatisfactory.\textsuperscript{21}

### Stable Perovskite-Polymer Composite Films via Swelling-deswelling Microencapsulations

A microencapsulation strategy has recently been developed by the authors’ team to achieve well-dispersed, intimately passivated OIP (CH\textsubscript{3}NH\textsubscript{3}PbX\textsubscript{3}, MAPbBr\textsubscript{3}) nanoparticles inside polymer matrices. This formulation could lead to OIP-polymer composite films with high photoluminescence efficiency, color purity, and ultra-high stability against heat and water exposure.\textsuperscript{22}

This strategy takes advantage of the well-known swelling-deswelling phenomenon in

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**Fig. 3:** In (a), an optical photograph (top left) shows suspensions of mixed halide MAPbX\textsubscript{3} (X being I, Br, or Cl) perovskites under visible and UV light, with (b) their corresponding PL spectra.\textsuperscript{14} In (c) (top center) an optical photograph shows suspensions of mixed halide CsPbX\textsubscript{3} (X being I, Br, or Cl) perovskites under UV light with (d) their corresponding PL spectra, and (e) typical optical absorption and PL spectra.\textsuperscript{16}
polymer physics. When brought into contact with good solvents, polymer chains will swell and expand, letting in solvents and solutes. Such expansion is generally reversible through a deswelling process, when the solvent is evaporated. OIP precursors can be introduced into polymer matrices as solute through the solvent-induced polymer swelling process. When the solvent is driven out of the polymer matrix (e.g. by heating), the OIP precursors will be left within the matrix to react and form high-quality, well-dispersed OIP nanoparticles. Meanwhile, the polymer matrix will deswell, shrink back, and form a coherent barrier layer around the OIP nanoparticles, protecting them from water, oxygen, or heat in the surrounding environment [Fig. 4(a)].

This strategy was demonstrated to be general, effective, and robust. A series of technically important polymer substrates (including polystyrene (PS), polycarbonate (PC), acrylonitrile butadiene styrene (ABS), etc.,) that swell in dimethylformamide solvent can be easily converted into highly luminescent OIP-polymer composite films through either cotton swab painting [Fig. 4(b)] or spin coating [Fig. 4(c)] of OIP precursor solutions. These composite films show high photoluminescence quantum yield (PLQY) of up to 48% and superior color purity owing to FWHM as small as 18 nm (narrower than even the best-performing CdSe-based green QDs).

Most importantly, these OIP-polymer composite films possess unprecedented water and heat stability. Some OIP-polymer composite films (MAPbBr3-PS, MAPbBr3-PC, and MAPbBr3-ABS films) can be immersed directly in water for two months, and experience less than 7% reduction of PLQY, indicating significant water stability [Fig. 4(d)]. Among them, MAPbBr3-PS and MAPbBr3-PC composite films can survive boiling.

Fig. 4: Above appears the swelling-deswelling microencapsulation strategy for OIP-polymer composite films. In (a) is a scheme of MAPbBr3—a polymer composite film formation process through swelling-deswelling (the inset shows a typical emission spectrum of as-prepared films). In (b) and (c) are images of the luminescent composite samples prepared by cotton swab painting (b) or spin coating (c) under UV excitation (365 nm). Samples from left to right are MAPbBr3-PS, MAPbBr3-PC, MAPbBr3-ABS, MAPbBr3-CA, MAPbBr3-PVC, and MAPbBr3-PMMA respectively. In (d) are shown stability characterizations of the composite film samples (MAPbBr3-PS, MAPbBr3-PC and MAPbBr3-ABS) immersed in water.
water treatment for 30 minutes with PLQY degradation of less than 15% and 7%, respectively, indicating high thermal and water stabilities even without any special barrier layer protection.22

Compared to Cd-based QDs, these perovskite-polymer composite films show clear advantages in terms of simpler processing (thus potentially lower cost), better color purity, and lower toxicity (according to RoHS regulations, the allowable concentration limit for Pb is 1,000 ppm, one order higher than that for Cd). Further investigations of PL efficiency and long-term stability under high optical flux conditions are needed to estimate their potential as a lower-cost, yet better-performing alternative to the green QD downconverters used in today’s QD-enhanced LCDs.

Photoluminescent Perovskites Work with QDs or Phosphors for LCD Backlights

While perovskite materials emitting other colors are under active development, the outstanding green perovskite-polymer composite films could work synergistically with other red downconverters in the near future. Besides CdSe- or InP-based red QDs, various narrow-band red phosphors could also be their good partners. Specifically, a K$_2$SiF$_6$:Mn$^{4+}$ (KSF/PFS) phosphor has been demonstrated to be a red downconverter with narrow emission peaks centered at 631 nm, with high conversion efficiency and high stability that could enable on-chip LED integrations. Recently, KSF/PFS phosphors have been commercialized by GE under RadiantRed and TriGain trademarks and have started to be adopted by major customers in the display and lighting industries.23,24 Another narrowband red phosphor (Sr[LiAl$_3$N$_4$]:Eu$^{2+}$, SLA) with longer emission wavelength also exhibits an exceptional stability.25 In the following section, we will discuss two configuration options in which these red downconverters could work with green perovskite-polymer composite films for LCD backlight unit (BLU) applications, and analyze the potential color gamut performance gains in these configurations.

Three commonly used downconverter backlight geometries are “on-chip,” “on-edge,” and “on-surface”.26 With simple, large-area processability and low cost, perovskite-polymer composite films are ideally suited for “on-surface” configuration. With high thermal stability, KSF/PFS or SLA phosphors can be applied in an “on-chip” configuration. For

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**Fig. 5:** The integration of perovskite-polymer composite films is shown with various red downconverters. Above are backlight system configurations for: (a) blue LED + green OIP + red QDs; (b) blue LED + green OIP + red phosphor (or red QDs in future); (c) the spectra of primary colors used for calculation; and (d) RGB color primaries in CIE 1931. Rec.2020 is plotted for reference. Insets on the right show relative positions of different red emitters.
QDs, while all three configurations have been reported, the currently commercialized products use “on-surface” configuration, and are called quantum dot enhancement films (QDEFs). Thus, the combination of green perovskite-polymer composite films and QD or phosphor can be carried out in the following two geometries:

1. Blue LED with on-surface green OIP above red QDs. Fig. 5(a) shows the configuration of “back-to-back” green OIP/red QDs film pumped by blue LED. In terms of reducing reabsorption and enhancing the photoluminescence, the layered structure with green emitters on top of red emitters was found to be more effective. Considering their wavelength tunability, QD spectra with a series of peak wavelengths (630, 635, 640 nm) have been analyzed.

2. Blue LED with on-chip red KSF/PFS phosphor/red SLA phosphor and on-surface green OIP [Fig. 5(b)]. Fig. 5(c) shows the spectra of high-power blue LED, green OIP-polymer composite film, and red QDs or phosphors. Their respective positions in the CIE 1931 have been marked in Fig. 5(d).

Table 1 lists the analysis results of color gamut coverage and total light efficiencies (TLEs) when a commercial color filter and liquid-crystal system are taken into consideration.26 Clearly, in order to gain wide color gamut while maintaining a moderate TLE, BLUs with green OIP-polymer composite films and 630-nm QDs or KSF phosphor are ideal choices, with nearly 90% Rec.2020 and around 20 lumens-per-watt efficiency. Among these, the combination of on-chip KSF phosphor and on-surface perovskite-polymer film are particularly promising for low-cost, efficient, color-vivid, and cadmium-free BLUs for LCDs.

Table 1. Below are the Rec.2020 color gamut coverages in CIE 1931 and total light efficiencies (TLEs) of several proposed configurations.

<table>
<thead>
<tr>
<th>BLU Red Emitter Choice</th>
<th>No LC/CF</th>
<th>With CF</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Rec.2020</td>
<td>Rec.2020</td>
</tr>
<tr>
<td>QDs 630nm</td>
<td>88.7%</td>
<td>89.6%</td>
</tr>
<tr>
<td>QDs 635nm</td>
<td>89.5%</td>
<td>90.5%</td>
</tr>
<tr>
<td>QDs 640nm</td>
<td>90.0%</td>
<td>91.2%</td>
</tr>
<tr>
<td>KSF Phosphor</td>
<td>88.2%</td>
<td>81.7%</td>
</tr>
<tr>
<td>SLA Phosphor</td>
<td>89.7%</td>
<td>85.2%</td>
</tr>
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</table>

PeLEDs and QLEDs: Development Status Varies for Different Colors

With the upsurge of perovskite solar cell research, PeLEDs have been revisited in the past several years in either forward28 or inverted29,30 OLED structures, and even in single-layer, light-emitting electrochemical cell structures.31 For PeLEDs with colors in display-relevant regions, green devices are the most developed, with demonstrated efficiencies of 42.9 Cd/A28. However, it should be noted that very few papers have reported lifetime data for PeLED devices, suggesting that reliability remains one big challenge for PeLEDs that needs to be addressed before the introduction of these technologies.26,27
technology can be developed into something of broader industrial interest. For further details on PeLED developments, interested readers can turn to several recent review papers.32–34 QLEDs are widely regarded as the next generation of self-emissive displays after OLEDs. Samsung’s recent acquisition of QD Vision has been taken as a signal of the company’s dedication to QDs and strong interest in QLEDs.35 Among QLEDs with visible colors,36–40 red QDs are currently the most developed in EL devices. Solution-processed CdSe-based red QLEDs have demonstrated efficiency and luminance that rival or beat state-of-the-art thermal-evaporated red OLEDs, with narrow peak linewidths in the 20- to 30-nm range.36,37,40 In contrast, green and blue QLEDs remain inferior to their OLED counterparts.38,39 This is partly because of the size-dependent quantum confinement effect; i.e., red QDs usually have the biggest size among QDs of all visible colors and can tolerate relatively large absolute size variation while still maintaining a tight percentage distribution, thus high color quality and efficiency.

In particular, the authors recently developed ultra-bright and efficient deep red CdSe-based quantum dot light-emitting devices (QLEDs).40 The device EL spectrum shows an FWHM of only 22 nm at CIE coordinates of (0.69, 0.31). More importantly, these devices achieved high peak current efficiency (20.5 Cd/A at ~20,000 Cd/m² with a driving voltage of only 3.5 V), high luminous power efficiency (with a peak level of 20.8 Lm/W) and small efficiency roll-off at high driving current density (Fig. 6). Ultra-high luminance of 165,000 Cd/m² was achieved at a current density of 1000 mA/cm² with a driving voltage as low as 5.8 V, which sets a new luminance record for existing organic-related, red, light-emitting devices.

Hybrid White OLED with Narrow Red QD Emitters for Lighting

Considering the demonstrated merits and existing challenges of QLEDs and PeLEDs, it will be difficult for them to displace OLEDs completely in the near future. Instead, a hybrid device that could integrate the advantageous QD or perovskite components with existing OLEDs will probably be a viable technology.
entry point for these materials to enter the display or lighting industry.

State-of-the-art white OLEDs (WOLEDs) use organic emitters for all colors and cannot achieve simultaneously high luminous efficacy and good color quality primarily due to the absence of organic emitters with narrow red emission peaks. Integrating narrow red-emitting QDs with organic blue and green emitters will help solve this problem. The integration could be based on tandem multi-stack structures (as in the all-organic WOLEDs from LG Display) or on a single-stack device structure in which emitters of different colors share the same electron/hole injection or transport layers. Figure 5 analyzes the potential benefit of replacing an existing red organic emitter in a single-stack WOLED device with red QDs’ narrow spectra of different intensity or peak wavelength choices. The resultant spectra have been analyzed for the enhancement of three key solid-state lighting performance metrics: the Color Rendering Index (CRI), and R9, and luminous efficacy of radiation (LER), and then compared to the original OLED’s performance.

As shown separately in Fig. 7 (a), (b), and (c), each of these metrics can reach a very high value (with LERpeak = 387.5 lm/W, CRIpeak = 91, and R9 peak = 97) by simply tuning the peak wavelength and relative intensity of red QDs gives the resulting hybrid WOLED system the flexibility to achieve different color or efficiency targets with the same organic emitter materials. So as long as their respective emission properties can be well reserved in the hybrid system, integrating red QDs into WOLED emitters will bring breakthroughs to the efficiency and color performances of OLED-based solid-state lighting.

In addition, it should be noted that this hybrid WOLED concept will provide a hybrid device platform for future developments. Novel materials, such as long-lifetime, high-efficiency, thermally activated, delayed-fluorescence (TADF) blue organic emitters, as discussed in another article in this issue, could be integrated into this platform in the future, leading to further performance improvements.

**Table 2. Performance improvements can be realized by replacing the existing red organic emitter with the narrow-band red spectra of QDs [A and B as marked in spectra of Fig. 7 (d) and (e)].**

<table>
<thead>
<tr>
<th></th>
<th>LER [lm/W]</th>
<th>CRI</th>
<th>R9</th>
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<tbody>
<tr>
<td>WOLED</td>
<td>341</td>
<td>82</td>
<td>-15</td>
</tr>
<tr>
<td>A</td>
<td>349</td>
<td>90</td>
<td>81</td>
</tr>
<tr>
<td>B</td>
<td>359</td>
<td>91</td>
<td>32</td>
</tr>
<tr>
<td>All organic WOLED by LG Display</td>
<td>328</td>
<td>89</td>
<td>31</td>
</tr>
<tr>
<td>All QD WOLED</td>
<td>296</td>
<td>93</td>
<td>75</td>
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**An Hybrid Future**

As emerging solution-processable luminescent nanomaterials, QDs and perovskites have outstanding merits of tunable color with high purity and high efficiency, but still suffer from stability issues for certain colors. Hybridization of these exciting new components with state-of-the-art phosphor or organic materials in PL or EL modes could accelerate their adoption in the near term and favorably impact the display and lighting markets.

**References**


