Tailoring the Spectrum

Low-Cost Perovskite-Polymer Composites

As solid-state lighting becomes smarter and strives for more than saving energy, the ability to tailor the spectrum following specific requirements offers tremendous opportunities. Here, four authors from the University of Central Florida propose low-cost, light-diffusing perovskite-polymer composites to meet demand.

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WITH ITS LOWER POWER CONSUMPTION, LONGER LIFE-time, smaller size, higher brightness, and faster response time, solid-state lighting (SSL) based on white LEDs has gradually overtaken incandescent and fluorescent lighting sources in the last few decades.[1] Although researchers have devoted significant effort to improving its efficiency, they've also studied the biological impact of light on human beings, plants, and animals.[2,3] Now is the time for SSL manufacturers to aim beyond energy savings, and expand their focus to applications such as circadian or horticultural lighting. In that sense, tailoring the spectrum according to specific requirements will become increasingly crucial, as it will maximize the effectiveness of the lighting by ensuring the presence of necessary spectrum components and, in the meantime, reduce or omit unnecessary or even damaging portions of the spectrum. For instance, under ambient light, the intrinsically photosensitive retinal ganglion cells (ipRGCs) innervating the suprachiasmatic nucleus (SCN) can influence melatonin secretion, thereby affecting the circadian rhythm.[4] In reference to the experiments on light-induced melatonin suppression, Dietrich Gall proposed an "action spectrum" of the circadian effect, with a peak at blue wavelengths.[5] (Incidentally, an “action spectrum” means a response spectrum correlated to the circadian effect, in this case with a peak around 460 nanometers [nm].) Indeed, it is necessary to factor the circadian effect into future design considerations to achieve human circadian lighting.

With this in mind, here we examine current SSL solutions and, based on the tailored SSL requirements, we propose low-cost, light-diffusing perovskite-polymer composites as candidates for narrow-band, color-tunable emitters. Using spectral optimizations, we offer a circadian SSL solution with high efficiency and excellent color rendering by incorporating perovskite-polymer composites.

What SSL Currently Offers

Current SSL solutions can be roughly categorized into three classes. Phosphor-converted white LEDs (pc-WLEDs) are the first and most mainstream solution. The simple design and low cost make them ideal for general, static lighting. However, the phosphor’s broad spectral power distribution (SPD) is considered spectrally inefficient, because human eyes are most sensitive to green light with a peak at 555 nm (photopic vision), and the broad SPD causes a significant spillover of light into the deeper red where human vision is not very sensitive. Meanwhile, as SSL becomes smarter, it requires SPD dynamic tuning.[6,7] Although some existing proposals can tune the SPD of pc-WLEDs (by using, for example, an active color filter),[8,9] it is still energy-inefficient, with a rather limited SPD engineering degree of freedom.

An additional problem with pc-WLEDs is that they use an

LED die that emits deep blue light, and they create white light by down-converting some of the photon energy from the blue source into red, green, yellow, and so forth, in the phosphor. However, this process has some energy loss associated with it. When an emitted photon has less energy than an absorbed photon, the energy difference is known as a "Stokes shift."

The second solution, which is considered the ultimate solution, is to use color-mixed LEDs. We accomplish this by packaging LED dies together with different emitting colors; then we tune the overall SPD by adjusting the intensity ratio of each die. The bandwidth of individual dies can be as narrow as 20 nm, which is ideal for tailored SSL, with no energy wasted by a Stokes shift. However, the wall-plug efficiency of green and amber LEDs is still low, in what is known as the "green gap," and this requires extra optics to mix different colors well. In the future, establishing dominance in the market will require much effort on the challenging task of improving green and amber LEDs.

The third and intermediate solution is hybrid configurations. Similar to the color-mixed LEDs, emitters with different colors are packaged together and can be adjusted individually. But here, only blue and red LED dies are applied, and the "green gap" is circumvented by using blue LED-pumped downconverters. Although energy loss occurs from the Stokes shift, it is still far more efficient than current color-mixed LEDs.

To fulfill the requirements of narrow bandwidths and tunable colors, using traditional quantum dots (QDs) as down converters has shown promise for fine SPD tailoring, although their manufacturing costs remain high and their stability still requires more improvement. On the other hand, three-dimensional (3D) metal halide perovskite nanocrystals (PNCs) with a chemical formula of ABX$_3$ (A is Cs$^+$, CH$_3$NH$_3^+$, or CH(NH$_2$)^2; B is Pb^{2+} or Sn^{2+}; X is Cl$^-$, Br$^-$, or I$^-$) have also emerged as promising solar photovoltaic or light-emitting downconverter materials with high efficiency and outstanding color tunability.

Their emission spectra can be tuned over the entire visible band, mainly by varying the A, B cations or halide composition. PNCs have obtained a photoluminescence quantum yield (PLQY) larger than 90 percent in solution with narrow emission linewidths less than 20 nm.[10] Compared to traditional QDs, PNCs are much easier to fabricate and, as a result, the manufacturing cost is far less. However, things that are easy to make are usually also easy to break. A lack of long-term stability is one of the key issues impeding their practical application.

QUICK TAKE

Tailoring the spectrum according to specific requirements will become increasingly crucial, as it will maximize the effectiveness of the lighting by ensuring the presence of necessary spectrum components and reduce or omit unnecessary or even damaging portions of the spectrum.

Enter Light-Diffusing Perovskite-Polymer Composites

Initially developed PNCs are dispersed in solution, similar to traditional QDs. Often their instability is attributed to their low formation energy, highly dynamic binding in solution, and susceptibility to heat, moisture, oxygen, and light. To fulfill the

Fig 1.

(a) Schematic illustration of the light-diffusing perovskite-polymer composite fabrication process. (b) Images of synthesized, light-diffusing perovskite-polymer composites under ambient and ultraviolet (UV) excitation. IPA stands for isopropyl alcohol.

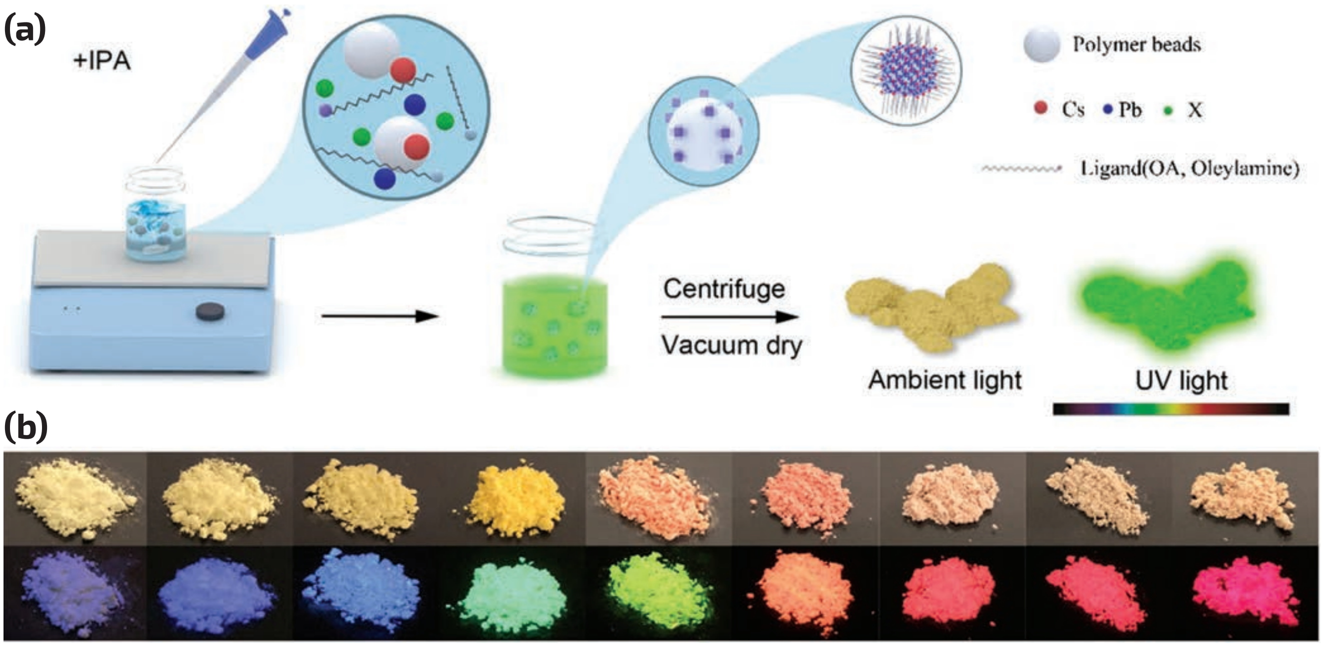


Fig. 1 reproduced from previous work[11] with permission from the Royal Society of Chemistry.

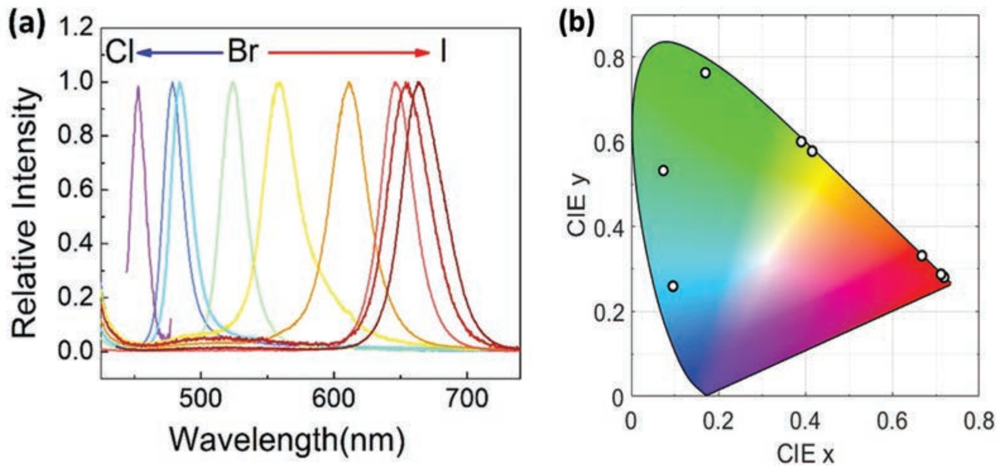


Fig. 2.

◄Optical properties of light-diffusing perovskite-polymer composites. (a) Photoluminescence spectrum of the samples under UV excitation. Chlorine, bromine, and iodine are represented as Cl, Br, and I. (b) Corresponding International Commission on Illumination (CIE) 1931 color coordinates of the samples under a blue LED excitation.

request for narrow-band, color-tunable, low-cost, and stable downconverters, our group recently developed light-diffusing perovskite-polymer composites consisting of PNCs and polymer microspheres.[11]

Employing polymer substrates in the system leads to multiple advantages. First, because the polymer substrates protect the PNCs, this increases the PNCs' environmental stability. Second, the PNCs avoid aggregation—i.e., when nanocrystals bind together and have lower surface energy—because they are passivated and separated by polymer chains. Moreover, the PNCs themselves can hardly diffuse light, as their crystal sizes are usually less than visible wavelengths. So, when we embed the light-diffusing capability into the system by incorporating light-diffusing polymer microspheres, we lower the total cost and make the system more compact.

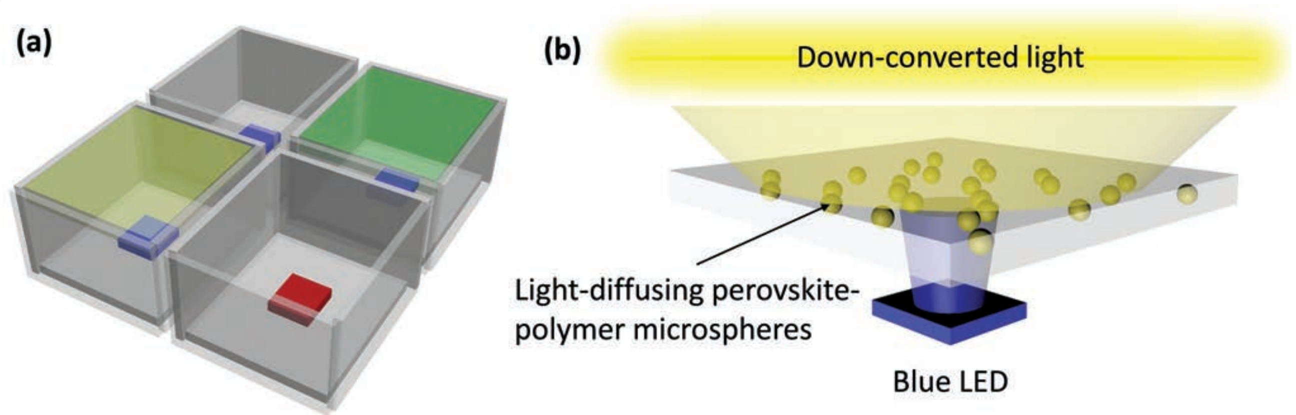
The synthesis of the light-diffusing perovskite-polymer composites only takes one step, and it is a general method that can convert commercial light-diffusing polymer microspheres into highly luminescent PNC-based downconverters at an extremely low cost. As **Fig. 1** schematically shows, commercial light-diffusing polymer microspheres were first dispersed in perovskite precursor solutions (CsX and PbX$_2$, X= Cl$^-$, Br$^-$, I$^-$) with a mixture of oleylamine (OAm) and oleic acid (OA) added as surfactants. Then, an antisolvent such as isopropyl alcohol (IPA) was quickly injected into the stirring dispersion to induce immediate perovskite nanocrystal nucleation onto the polymer microspheres. The formation of perovskite-polymer composites transpires within several seconds at room temperature. After further simple centrifugation and vacuum drying, we obtain light-diffusing, downconverting microspheres.

The process is generic and can be applied to CsPbX$_3$ precursor solutions with different halide components X (chlorine [Cl], bromine [Br], and iodine [I]) to achieve widely tunable bandgaps. As **Fig. 1(b)** shows, we can synthesize a series of CsPbX$_3$-polymer samples through a simple anion tuning, where vivid colors are observed under UV exposure. As expected, the CsPbBr$_3$ sample exhibits pure green emission. By increasing the stoichiometry ratio of chloride and iodine precursors, we can shift the emission to shorter and longer wavelengths, respectively, and cover the entire visible range.

Optical characterizations reveal the outstanding color purity and tunability of these perovskite-polymer compos-

Fig. 3.

▼(a) Schematic illustration of the RYGB hybrid configuration. (b) Detailed illustration of how the light-diffusing perovskite-polymer microspheres are incorporated into the hybrid configuration.



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ites. Photoluminescent (PL) spectra of the samples and their corresponding CIE 1931 color coordinates are plotted in **Figs. 2(a)** and **2(b)**, respectively. The emission colors can be tuned from blue (453 nm) to deep red (662 nm) with a full width at half maxima (FWHM) ranging from 12.5 to 37 nm, which ensures highly saturated colors covering the entire visible band. Among them, the green-emitting $CsPbBr_3$-polymer microspheres manifest a high-PL quantum yield of 70.6 percent, and red-emitting $CsPbBr_xI_{3-x}$-polymer microspheres (x=0.75) manifest a PL quantum yield of 40.5 percent.

By combining PNCs with polymer microspheres, the as-synthesized perovskite-polymer composites are surprisingly stable in water. To test stability, we immersed $CsPbBr_3$-polymer microspheres in water and recorded their PL intensity every 24 hours. After being immersed for more than 50 days, the green samples maintained around 75–80 percent of their original PL intensity. Further tests show that the perovskite-polymer microspheres can even survive and remain luminescent in boiling water. Compared with neat PNCs that are quickly quenched in a water environment, the astonishing stability of the perovskite-polymer composites in water and heat makes them very promising for practical applications.

Using Spectral Optimizations for Efficiency, Color Rendering, and Circadian SSL

Once we have low-cost, narrow-band, color-tunable emitters, we can design SSL for specific applications. Here, we demonstrate the light-diffusing perovskite-polymer composites in a hybrid configuration for a high-efficiency, excellent color-rendering, circadian SSL solution.

In this hybrid configuration, four individually controlled emitters—namely, a blue LED, a green downconverter pumped by a blue LED, a yellow downconverter pumped by a blue LED, and a red LED (RYGB) are involved in the optimizations (**Fig. 3**). More emitters can provide a greater design degree of freedom, but inevitably, this increases the difficulties in designing the driving circuit and color-mixing optics. Our choice makes use of high-efficiency LEDs, avoids the "green gap," and provides a decent design degree of freedom. In the calculation, the FWHM of blue and red LEDs is set to 20 nm, while the FWHM of green and yellow downconverters is determined by the PNCs' intrinsic optical properties.[12] These four emitters' peak wavelengths also can vary.

A good circadian SSL solution should have high-vision energy efficiency, excellent color-rendering quality, and an appropriate circadian effect according to the correlated color temperature. For this purpose, we chose three targets, namely the luminous efficacy of radiation (LER), color-quality scale (CQS), and circadian action factor (CAF).

LER reflects the output light's efficiency that can be converted to brightness received by human eyes; it is solely dependent on spectral properties. For the color quality metric, instead of applying the frequently used color-rendering index (CRI), CQS is employed; this is far more suitable for narrow-band emitters,

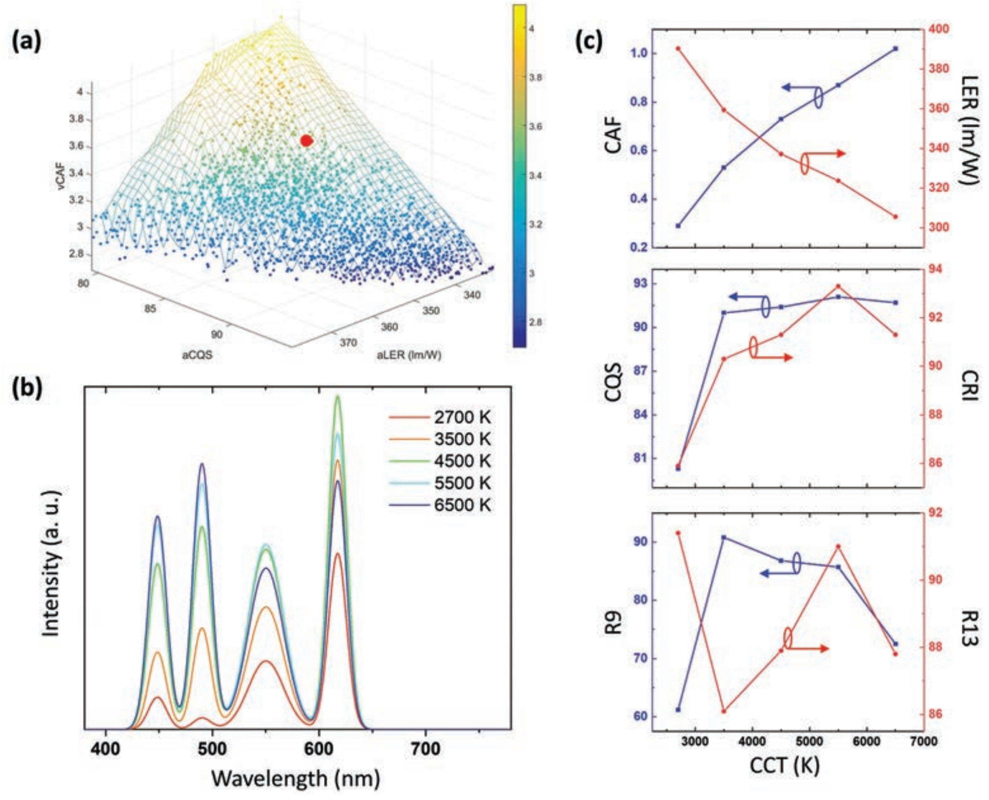

Fig 4.

(a) The Pareto front of the three-objective optimization for a tunable solid-state lighting (SSL) solution, where the red dot denotes optimal solution 1 (OP1). (b) Spectral power distribution (SPD) at variable CCTs. The peak wavelengths of the components are 448.5, 490.3, 550.3, and 617.3 nm. The bandwidths are 19.9 and 39.1 nm for green and yellow, respectively. (c) Details of the circadian action factor (CAF), luminous efficacy of radiation (LER), color-quality scale (CQS), color-rendering index (CRI), deep red (R9), and skin-tone (R13) values as a function of CCT.[12]

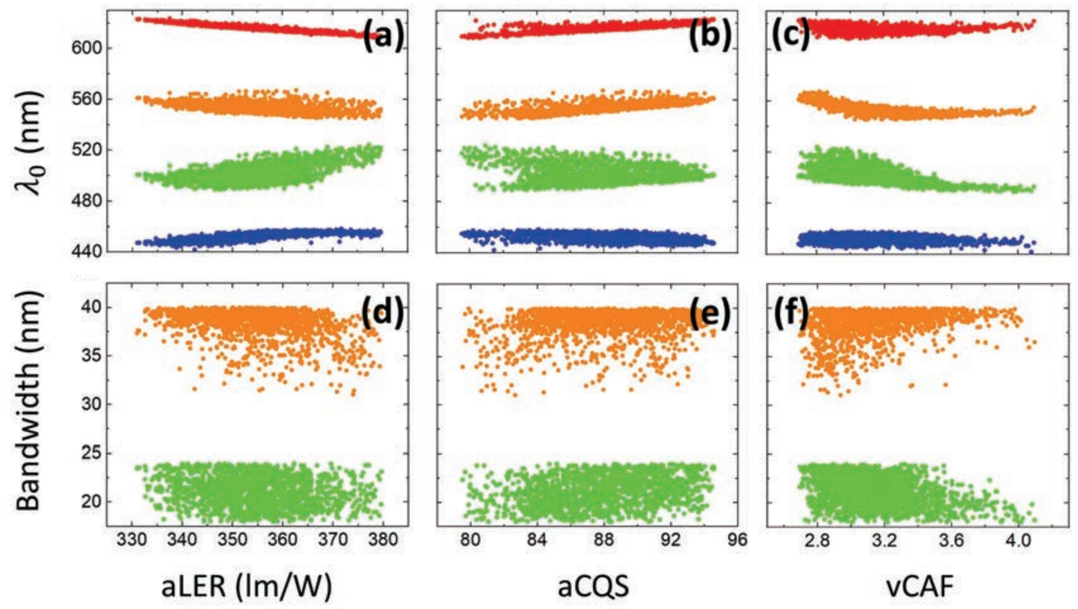

Fig. 5.

(a-c) Correlations between the objectives and central wavelengths of blue LED (blue), green film (green), yellow film (orange), and red LED (red); and (d-f) correlations between the objectives and bandwidths of a green downconverter (green) and yellow downconverter (orange) for CCT-tunable SSL solutions.[12]

and it outperforms in many respects.[13]

CAF characterizes light's circadian effect, which is calculated by integrating light's spectrum with the circadian action spectrum previously mentioned. With a higher value of CAF, light can make people feel more energetic and thus is suitable for a working environment. In contrast, a lower value is more suitable for evening or bedroom lighting that enables people to more easily fall asleep. (For calculation details, see related work.[12–14]) Here, we target circadian SSL solutions that change from a low (2,700 kelvins, or K) to high CCT (6,500 K). Thus, we define the objective functions as

$$\mathrm{vCAF}=\mathrm{CAF}_{6500\mathrm{K}}/\mathrm{CAF}_{2700\mathrm{K}} \qquad (1)$$

$$\mathrm{aLER}=(\mathrm{LER}_{2700\mathrm{K}}+\mathrm{LER}_{6500\mathrm{K}})/2 \qquad (2)$$

$$\mathrm{aCQS}=\sqrt{(\mathrm{CQS}^2_{2700\mathrm{K}}+\mathrm{CQS}^2_{6500\mathrm{K}})/2} \qquad (3)$$

After defining all the variables and objectives, we optimize performance. For general multiobjective optimizations, there will be tradeoffs between the objectives, resulting in a set of optimal solutions where each individual will have at least one objective outperforming others. Such a set of optimal solutions creates a Pareto front, as **Fig. 4(a)** shows. The three objectives are strongly mutually exclusive, which is evident by the triangular-like geometry. We select a special optimal solution (OP1) for detailed study, denoted as the red point in **Fig. 4(a)**. OP1 has 3.52 vCAF, 348.0 lumens per watt (lm/W) aLER and 86.2 aCQS (the corresponding standard illuminant has 2.78 vCAF, 176.0 lm/W aLER and 98.8 aCQS). Specifically, it provides 0.29 CAF, 390.5 lm/W LER and 80.3 CQS at 2,700 K and 1.02 CAF, 305.6 lm/W LER and 91.7 CQS at 6,500 K.

We further implement the intermediate CCTs, to ensure the tunability in between these two CCTs. Because there are more than three colors, we always can choose points that lie on the blackbody locus and fine-tune the intermediate CCTs' performance. **Fig. 4(b)** shows an example of SPD variation. **Fig. 4(c)** further demonstrates the details of CAF, LER, CQS, CRI, R9 (deep red), and R13 (skin tone) values as a function of CCTs. The optimized solution performs quite well in rendering deep red and skin-tone colors. Moreover, it can follow the circadian phase and offer lower and higher CAF than the corresponding standard illuminant at 2,700 and 6,500 K, respectively. Thus, this example is a perfect SSL source with large CAF tunability, high efficiency, and excellent color rendering.

An advantage of the systematic optimization is that it lets us study the parameter preference, as well as the correlations between each input parameter and objective. As plotted in **Fig. 5**, for a higher average LER, the red LED tends to have shorter central wavelengths, while the blue LED and green downconverter tend to have longer central wavelengths. In the meantime, the higher average CQS requires longer central wavelengths of the red LED and yellow downconverter. Interestingly, large CAF variability confines all four central wavelengths. This can be a guideline for designs of large CAF tunability with four-hump SSL sources. On the other hand, the bandwidths of the two downconverters do not show a strong correlation to the average LER and CQS. However, for large CAF tunability, the yellow emitter spectrum should be broad, while the green emitter spectrum should be narrow.

As SSL solutions continue to evolve, there is tremendous opportunity for the research community to embolden its vision and expand development. To meet the increasing needs of high-performance tailored lighting using the hybrid configuration, we developed light-diffusing perovskite-polymer composites through a simple antisolvent-induced heterogeneous nucleation process on commercial light-diffusing polymer microspheres. These composites demonstrate high stability, high efficiency, excellent color purity, and significant cost savings. So that they can be utilized further in specific lighting applications, we also performed spectral optimizations based on their optical properties. Taking circadian SSL as an example, we demonstrated the capability of configuring SSL solutions with a proper circadian effect, high efficiency, and excellent color rendering.

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References

[1] Crawford MH. LEDs for solid-state lighting: performance challenges and recent advances. IEEE J. of Selected Topics in Quantum Electronics. 2009;15(4):1028-40.

[2] Pattison PM et al. LEDs for photons, physiology and food. Nature. 2018;563(7732);493-500.

[3] Czeisler CA. Perspective: casting light on sleep deficiency. Nature. 2013;497:S13.

[4] Berson DM, Dunn FA, Takao M. Phototransduction by retinal ganglion cells that set the circadian clock. Science. 2002;295(5557): 1070-73.

[5] Gall D. Circadiane Lichtgrößen und deren messtechnische ermittlung Circadian light parameters and their metrological determination]. Licht [Light]. 2002;54:1292-97.

[6] Schubert EF, Kim JK. Solid-state light sources getting smart. Science. 2005;308(5726):1274-78.

[7] Tsao JY et al. Toward smart and ultra-efficient solid-state lighting. Advanced Optical Materials. 2014;2(9):809-36.

[8] Chen H et al. Tuning the correlated color temperature of white LED with a guest-host liquid crystal. Optics Express. 2015;23(10):13060-68.

[9] He Z et al. Tuning the correlated color temperature of white light-emitting diodes resembling Planckian locus. Optics Express. 2018;26:A136-43.

[10] Protesescu L et al. Nanocrystals of cesium lead halide perovskites (CsPbX3, X = Cl, Br, and I): novel optoelectronic materials showing bright emission with wide color gamut. Nano Letters. 2015;15(6): 3692-96.

[11] Zhang C et al. Light diffusing, down-converting perovskite-on-polymer microspheres. J. Materials Chemistry C. 2019;7:6527-33.

[12] He Z et al. Perovskite downconverters for efficient, excellent color-rendering, and circadian solid-state lighting. Nanomaterials. 2019;9(2):176.

[13] Ohno Y. Spectral design considerations for color rendering of white LED light sources. Optical Engineering. 2005;44(11):111302.

[14] He Z et al. Emerging perovskite nanocrystals-enhanced solid-state lighting and liquid-crystal displays. Crystals. 2019;9(2):59.