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Zong-Tao Li, Bo-Jia Li, Jia-Sheng Li, Cun-Jiang Song, Xin-Rui Ding, et al.. Utilizing internal resonant scattering to improve photoluminescence energy outcoupling of CsPbBr₃/Cs₄PbBr₆ perovskite phosphor. *Chemical Engineering Journal*, 2023, 476, pp.146457. 10.1016/j.cej.2023.146457 . hal-04273729

HAL Id: hal-04273729

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Submitted on 7 Nov 2023

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1 **Utilizing Internal Resonant Scattering to Improve Photoluminescence**
2 **Energy Outcoupling of CsPbBr₃/Cs₄PbBr₆ Perovskite Phosphor**

3

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21 **Abstract**

22 Although stable perovskite phosphors, i.e., CsPbBr₃/Cs₄PbBr₆, were
23 extensively reported and made great progress, achieving strong
24 photoluminescence (PL) energy outcoupling remains challenging owing to their
25 short Stoke's shift with serious PL energy absorption. This study utilized internal
26 resonant scattering (IRS) to improve the PL energy outcoupling (PEO) of
27 CsPbBr₃/Cs₄PbBr₆ perovskite phosphor, which was realized by the nanopore-
28 packing perovskite particles (NP-PPs) structure inside a phosphor. The nano-
29 porous matrix hybrid solid-liquid interfacial reaction was developed to construct
30 NP-PPs in a phosphor, and it is optimized to achieve a denser NP-PP structure
31 with an enhanced PEO effect (2.8-fold enhanced PL intensity). Numerical results
32 revealed that the NP-PP structure transforms the PL energy absorption mode to
33 the IRS mode, most of the scattering PL energy evades NP-PPs instead of
34 propagating inside. The optimized phosphor was applied to white devices, and we
35 finally achieved an ultrahigh luminous efficacy of 131.32 lm/W based on green
36 perovskite phosphors. This study provides a general guide for efficient perovskite
37 phosphors utilizing the nano-porous matrix to enable the IRS effect.

38

39 **Keywords:** CsPbBr₃/Cs₄PbBr₆ perovskite; light-emitting diode;

40 photoluminescence energy outcoupling; internal resonant scattering; efficiency

41

42

43 **1. Introduction**

44 Perovskite phosphors are promising as color converters in optoelectronic
45 devices, *i.e.*, light-emitting diodes (LEDs), because of their narrow band emission,
46 wide tunable bandgap, and high defect tolerance [1-7]. Since Kovalenko's group
47 first synthesize the nanocrystals of cesium lead halide perovskite CsPbX₃ [8],
48 great efforts have focused on improving the photoluminescence quantum yield
49 (PLQY) of perovskites phosphor. Nowadays, their PLQYs generally range from
50 85%-100% [9, 10], which is as high as mature phosphor materials including the
51 yttrium aluminum garnet:Ce phosphor, β-Sialon:Eu²⁺ phosphor, CdSe phosphor,
52 and so on [11, 12]. Recently, Zhong et al. indicated that the lifespan of perovskite
53 color converters has been largely improved to meet industry standards [13].
54 Especially, green composite perovskite phosphors composed of two or more
55 halide perovskite phases (Cs₄PbBr₆ and CsPbBr₃, CsPb₂Br₅ and CsPbBr₃, etc.)
56 perform remarkable stability in perovskite phosphors, as the CsPbBr₃ emitters are
57 well passivated by Cs₄PbBr₆ or CsPb₂Br₅ [14, 15], and thereby demonstrating a
58 superior durable high-power-driving capability at an ultrahigh working current of
59 300 mA [16]. Additionally, perovskite phosphors are necessary to achieve high
60 PL intensity to satisfy the luminous efficacy (LE) requirement of wide-color-
61 gamut white LEDs, which needs to advance toward the practical limit of 250
62 lm/W by 2035 [17]. Unfortunately, the PL intensity enhancement is limited by the
63 low PL energy outcoupling (PEO) of perovskite phosphors, leading to the
64 disappointing LE of white LEDs (generally < 90 lm/W [18, 19]), although they

65 have great PLQY compared with mature rare-earth and CdSe phosphors (> 200
66 lm/W) [20]. Therefore, improving the PEO is necessary and challenging, which
67 becomes a bottleneck for the application of perovskite phosphors in efficient
68 wide-color gamut white devices [21-23].

69

70 The low PEO of perovskite phosphors is generally attributed to the short
71 Stokes' shift [24], the PL energy emitting from a perovskite phosphor is easily
72 absorbed by perovskite phosphors themselves, especially when the device have a
73 high optical density of perovskite phosphors [25]. What is worse, the high surface
74 energy of perovskite particles leads to easy aggregation. The aggregated large-size
75 particle has a long light path of PL photons and leads to a so-called aggregation-
76 induced PL energy absorption [26, 27]. Therefore, previous studies mainly
77 focused on reducing the aggregation of perovskite particles for the PEO
78 improvement. For examples, dispersing matrices (e.g., nanocelluloses [28],
79 polymer frameworks [29], diatomite [30], silica spheres [31, 32] and metal-
80 organic frameworks [33-35]) are widely utilized to suppress the aggregation of
81 perovskite particles through physical or chemical integration. As for a less-
82 aggregated discrete perovskite particle (DPP) with smaller size and shorter optical
83 path, the PL energy suffers from a lower absorption before escaping to the matrix
84 [36]. As for a multiple perovskite particles (MPP) system, the escaping PL energy
85 further suffers from serious absorption by a great amount of other perovskite
86 particles in the matrix [25], and the PEO mechanism is still unclear. Especially,

87 previous studies almost concentrated on naturally unstable single-phase perovskite
88 phosphors, the dispersing matrices are also well designed to ensure the high
89 stability of perovskite phosphors, such as introducing dense ligands [37, 38],
90 protective layers [23, 34], and so on, which further aggravates the PL energy
91 absorption. As mentioned above, the CsPbBr₃/Cs₄PbBr₆ perovskite phosphor is
92 with high stability, as well as its simple structure mainly occupied by the
93 Cs₄PbBr₆ without ligand modification, showing great potential to achieve high
94 PEO, while its *in-situ* synthesis in a dispersing matrix and the PEO enhanced
95 mechanism are barely concerned.

96
97 In this study, we utilized internal resonant scattering (IRS) to improve the
98 PEO of CsPbBr₃/Cs₄PbBr₆ perovskite phosphor, which was realized by the
99 nanopore-packing perovskite particles (NP-PPs) inside a phosphor. A nano-
100 porous matrix hybrid solid-liquid interfacial (NMHS-LI) reaction was developed
101 to prepare the NP-PP phosphor, and the key parameters including ultrasonic
102 power and matrix content were optimized to achieve the NP-PP phosphor with
103 improved PL intensity. A finite-difference time-domain (FDTD) model was
104 introduced to confirm the enhanced PEO of NP-PP phosphor, demonstrating an
105 IRS effect to suppress the PL energy absorption for the MPP system. The
106 optimized phosphor was finally applied to the white LEDs, achieving an ultrahigh
107 LE of 131.32 lm/W based on green perovskite phosphors, which is much higher
108 than that in common reports. This strategy provides a general guide for highly

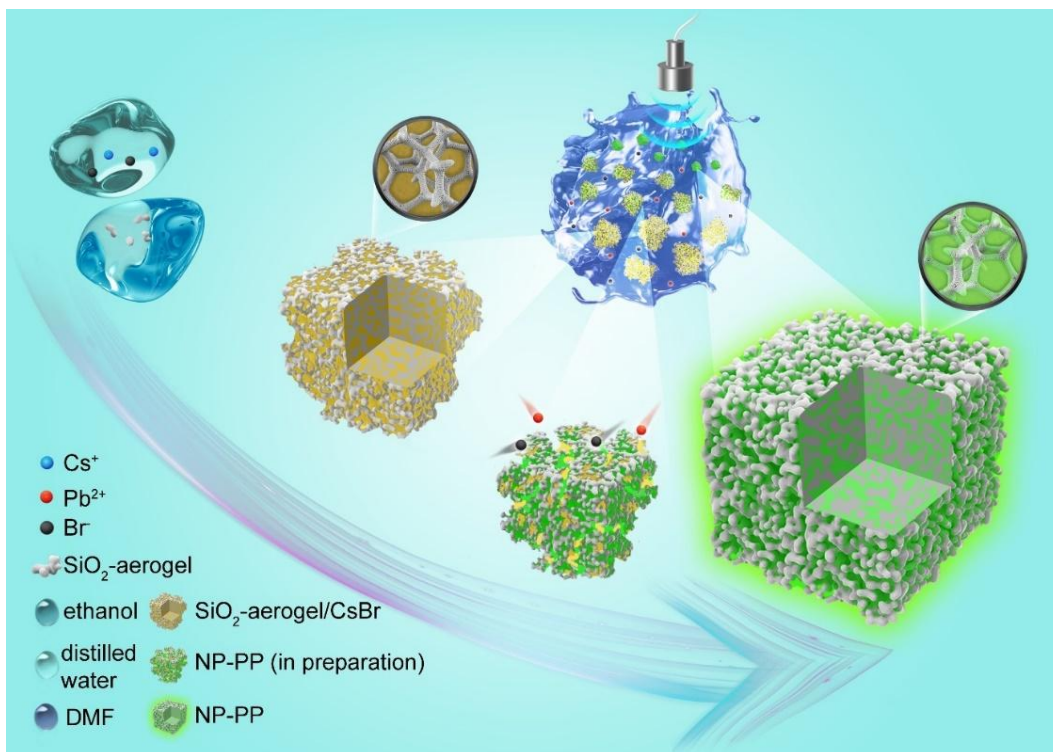
109 efficient and stable perovskite phosphors utilizing nano-porous matrices.

110 **2. Results and discussion**

111 *2.1 NP-PP Phosphor Preparation*

112 Herein, a hydrophobic SiO₂-aerogel was selected as a nano-porous matrix to
113 construct the NP-PP structure in a CsPbBr₃/Cs₄PbBr₆ perovskite phosphor.
114 Reasons are as follows: 1) its open porous network with moderate nanopores (20-
115 80 nm) is helpful for the solid precursor fully integration with the matrix; 2) such
116 a size range of nanopores is helpful to avoid the PL energy absorption in a
117 perovskite particle, and its low refractive index for visible light is enough to
118 enable the IRS effect, which will be discussed at the subsequent numerical study;
119 3) its hydrophobic nanorough surface can avoid the large aggregation among NP-
120 PP phosphors, and also help to resist water and oxygen erosion. Accordingly, we
121 developed a NMHS-LI reaction method to preparing the NP-PP phosphor, as
122 shown in **Fig. 1**. Firstly, the SiO₂-aerogel/CsBr hybrid solid precursor was
123 prepared for subsequent reaction. The hydrophobic aerogel was uniformly
124 dispersed into an ethanol solvent, and then mixed with hydrophilic CsBr in water
125 (**Fig. S1**). After the facile wet-mixing and evaporation process, a hybrid solid
126 precursor with CsBr particles embedded in the aerogel matrix was obtained (**Fig.**
127 **S2**) owing to the recrystallization of CsBr particles inside the nanopores of the
128 aerogel. Next, after grinding, excessive hybrid solid precursors were added to the
129 liquid precursor of PbBr₂ in DMF solvent. Herein, we utilized the efficient
130 ultrasonication to provide reaction energy for the solid-liquid interface reaction

131 instead of heating as previous study [39], as the ultrasonication can largely reduce
132 the process time (less than half an hour) and improved the dispersity of particles.
133 During the NMHS-LI reaction, the PbBr_2 precursors were dissolved in DMF; the
134 SiO_2 -aerogel/CsBr hybrid precursors were just broken with their aerogel matrix
135 structure kept, owing to the insolubility of CsBr and SiO_2 in DMF. Additionally,
136 the matrix structure provided numerous reaction sites for perovskite synthesis.
137 Therefore, these conditions enabled the Pb^{2+} ions to *in-situ* synthesize NP-PP
138 phosphor on the matrix with the hybrid precursors. The Pb:Cs ratio was optimized
139 to 1:6 for achieving the maximum PLQY (38.6%) of $\text{CsPbBr}_3/\text{Cs}_4\text{PbBr}_6$ phosphor
140 without dispersing matrix, which was also used as the controlled group (called as
141 pure perovskite phosphors), and details of which can be found in **Fig. S3**. During
142 the NMHS-LI reaction, the hybrid solids at the bottom of the DMF solvent
143 changed from orange to yellow-green (**Fig. S4**), indicating that the NP-PP
144 phosphor was synthesized. As our NP-PP phosphor was entirely ligand-free, the
145 ligand shedding was out of consideration [40], and the product can be transferred
146 to a highly volatile organic solvent (n-hexane) for rapid drying within several
147 minutes, and then easily achieving the solid-state NP-PP phosphor.



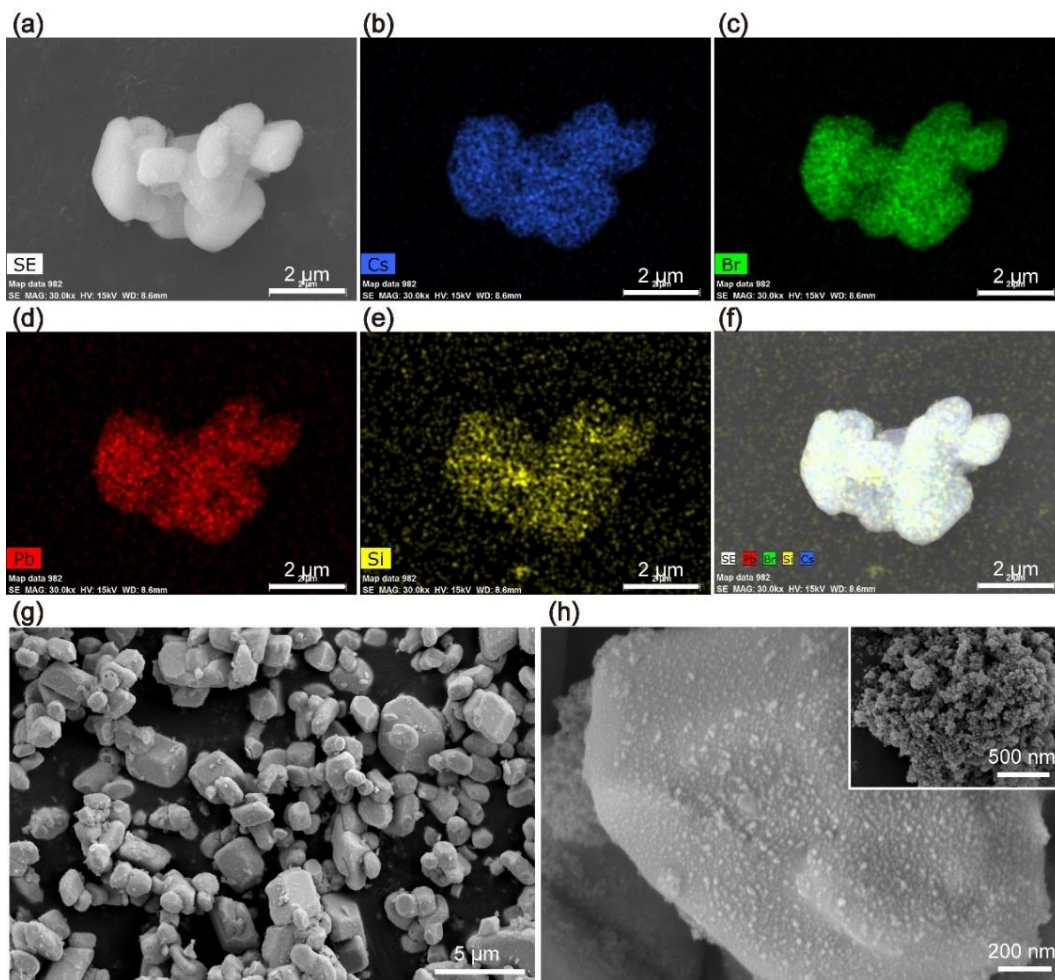
148

149 **Fig. 1. In-situ synthesis process of NP-PP phosphor via the NMHS-LI**
 150 **reaction.**

151

152 To confirm the successful synthesis of the NP-PP phosphor, its scanning
 153 electron microscopy (SEM) morphology was analyzed, as shown in **Fig. 2**. The
 154 ultrasonic power and matrix content were maintained at 40 W and 3.5 wt%,
 155 respectively; these two key factors will be discussed in detail subsequently. **Fig.**
 156 **2a-f** show the morphology of NP-PP phosphor and its elemental mapping. The Si
 157 originates from the aerogel matrix, whereas the Cs, Pb, and Br are from perovskite
 158 nanocrystals. These elements overlap greatly, demonstrating a uniform NMHS-LI
 159 reaction in the NP-PP phosphor. To confirm the uniform distribution of NP-PPs in

160 the internal region of the aerogel matrix, elemental mappings of the cross-
161 sectional phosphor were obtained using focused ion beam (FIB) cutting (**Fig. S5**).
162 And the high-resolution Transmission electron microscope (TEM) images also
163 verify that the perovskite nanocrystals were synthesized in the matrix (**Fig. S6**).
164 Additionally, the surface and cross-sectional morphologies of the NP-PP phosphor
165 were investigated, as shown in **Fig. 2g** and **Fig. S7**, respectively. This phosphor
166 presented a nanorough surface, originating from the nano-porous structure of the
167 aerogel matrix, which can be further supported by the smooth surface of the pure
168 perovskite phosphor without an aerogel matrix *in-situ* encapsulant (**Fig. S8**).



169

170 **Fig. 2. Morphology of NP-PP phosphor.** (a) SEM image of NP-PP phosphor for
 171 element mapping. (b)-(f) Element mappings of Si, Cs, Br, Pb, and their
 172 composites, respectively. (g)-(h) SEM images of NP-PP phosphor at a different
 173 magnification. Inset: SEM image of an aerogel matrix.

174

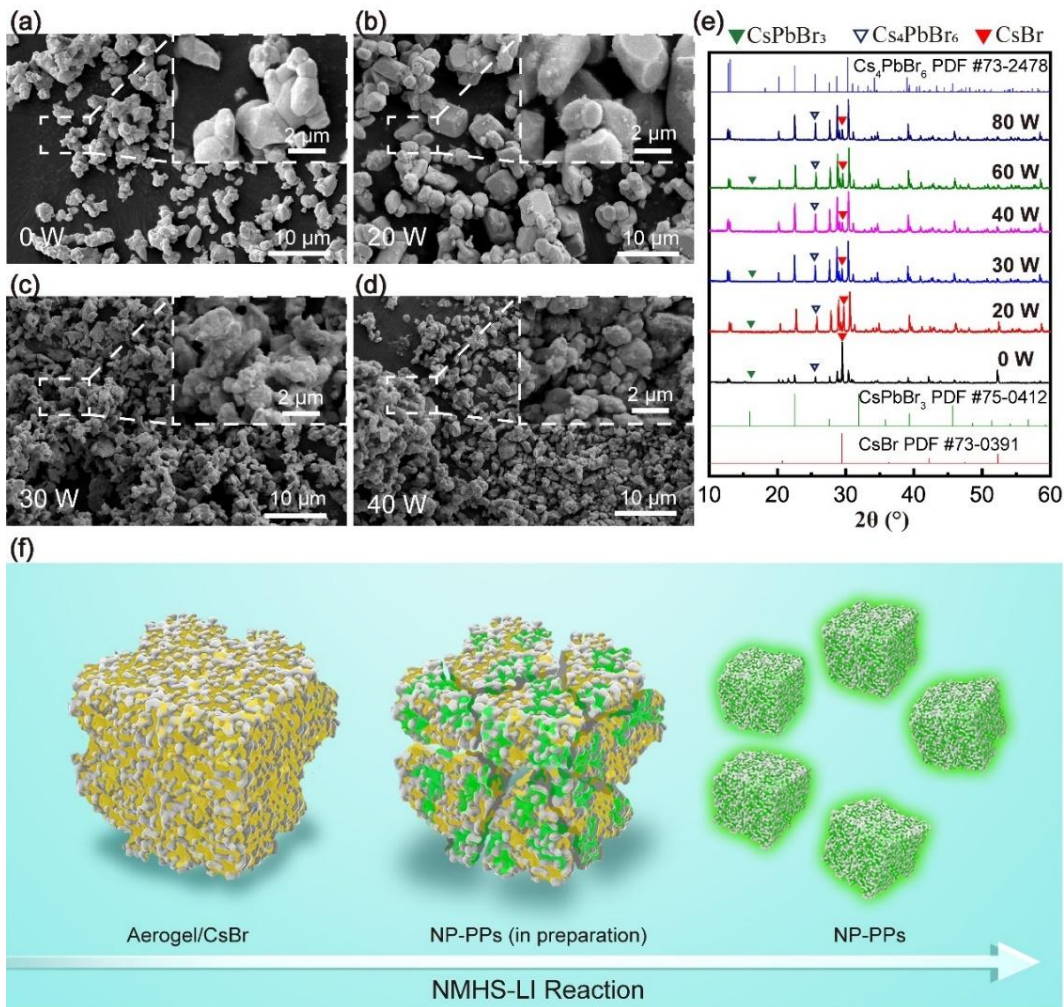
175 2.2 Structure Optimization of NP-PP phosphor

176 2.2.1 Morphology and dispersity

177 The NP-PP structure was ensured to be well *in-situ* synthesized inside the

178 phosphor by optimizing the ultrasonic power and matrix content, which are two
179 key factors of the NMHS-LI reaction process. For the first key parameter, external
180 energy provides activation energy for the chemical reaction [39]; and the
181 ultrasonic power breaks up both the precursor particles and aggregated particles,
182 which refines the products and accelerates the synthesis [41, 42]. Therefore, the
183 ultrasonic power has great impacts on the NMHS-LI. For the second key
184 parameter, the SiO₂-aerogel matrix provides its nano porous structure for the NP-
185 PP phosphor. The higher the matrix content, the denser the NP-PP structure,
186 which significantly affects their optical properties. Above two impacts will be
187 discussed later. The SEM morphologies of the NP-PP phosphor at different
188 ultrasonic powers are shown in **Fig. 3a-d**. We found that NP-PP phosphor
189 particles without ultrasonication were smaller than that of the hybrid solid
190 precursors of SiO₂-aerogel/CsBr. This means that the supersaturated hybrid solid
191 precursors were locally broken in NMHS-LI reaction to crystallized into
192 perovskite crystals. Moreover, the particle size of the NP-PP phosphor decreased
193 as the ultrasonic power increased from 0 to 40 W, with a reduction in mean
194 particle size from 2.7 to 1.7 μm (**Fig. S9**). To have a deep understand, the X-ray
195 diffraction (XRD) patterns were provided in **Fig. 3e** for Qualitative analysis. We
196 found that the enhanced ultrasonic power also helps accelerate the NMHS-LI
197 reaction, which was exhibited by the decreased CsBr peak in the X-ray diffraction
198 (XRD) patterns. Moreover, the XRD patterns (CsBr and Cs₄PbBr₆ peaks) of the
199 phosphor were almost unchanged after the ultrasonic power reached 30 W,

200 demonstrating that the NMHS-LI reaction of constructing NP-PPs was nearly
201 complete. These results indicate that the synthetic NP-PP phosphor has good
202 rigidity and is difficult to further dissociate by ultrasonication, and the
203 dissociation of hybrid solid precursors occurs during the reaction as shown in **Fig.**
204 **3f**. As a result, the dissociation and reaction of the hybrid solid precursors are
205 competitive with enhanced ultrasonic power, leading to a larger phosphor size
206 with an excess ultrasonic power of over 40 W (**Fig. S10**). Nevertheless, the
207 suitable ultrasonic power (~40 W in our case) is helpful for achieving the
208 complete NP-PP structure with a concentrated and small size distribution.

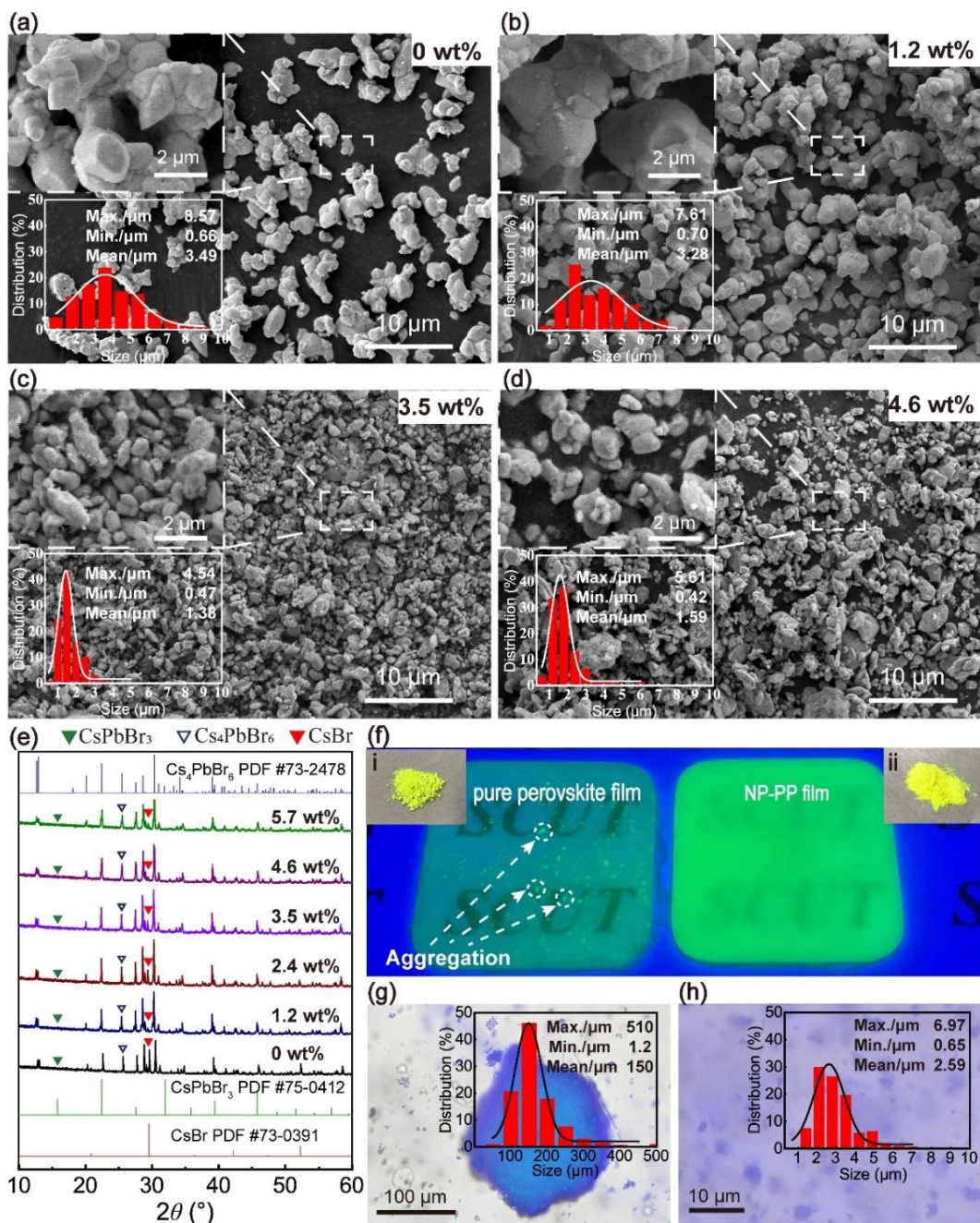


209

210 **Fig. 3. Effect of ultrasonic power on the particle structure of NP-PP**
 211 **phosphor.** (a)-(d) SEM morphology of NP-PP phosphor at ultrasonic powers of 0,
 212 20, 30, and 40 W, respectively. (e) XRD patterns of NP-PP phosphor at different
 213 ultrasonic powers. (f) Diagram of dynamic processes of the seed dissociation and
 214 reaction under NMHS-LI reaction. The matrix content was 3.5 wt% for all
 215 samples.

216

217 The matrix content is the other key factor influencing the NP-PP structure, as
218 shown in **Fig. 4a-d**. The pure perovskite phosphor without the aerogel matrix had
219 a larger size than the NP-PP phosphor, indicating that the introduced matrix, with
220 a large surface area for solvent interaction, was also beneficial to the dissociation
221 of supersaturated hybrid solid precursors. Furthermore, we found that the
222 phosphor size increased with an increase in matrix content; a larger size of 2 μm
223 was observed as the matrix content increased to 5.7 wt% (**Fig. S11**). These results
224 can also be explained by the accelerated reaction resulting from the increase in
225 matrix content. Interestingly, the XRD peak of CsBr clearly decreased after
226 introducing the matrix, as shown in **Fig. 4e**, indicating that the enhanced matrix
227 content also helps to obtain the NP-PP structure. One possibility is that the nano
228 porous structure of the SiO_2 -aerogel/CsBr seed, with a larger surface area,
229 provides many more reaction sites for the CsBr in hybrid solid precursors and
230 PbBr_2 in liquid precursors compared with the pure CsBr solid. Therefore, the
231 dissociation and reaction of hybrid solid precursors are also competitive with
232 increasing matrix content, reaching the optimal NP-PP structure and minimum
233 mean size of 1.4 μm at a matrix content of 3.5 wt%, which is smaller than that of
234 the pure perovskite phosphor (mean size = 3.5 μm).



235

236 **Fig. 4. Effect of matrix content on the particle structure of NP-PP phosphor.**

237 (a)-(d) SEM morphology of NP-PP phosphor with matrix contents of 0, 1.2, 3.5,

238 and 4.6 wt%, respectively. The inserted cartograms show the corresponding

239 particle distribution. (e) XRD patterns of NP-PP phosphor with different matrix
240 contents. (f) Photographs of pure perovskite and NP-PP films under UV
241 irradiance, respectively. The insets are the images of (i) pure perovskite and (ii)
242 NP-PP phosphors, respectively. (g-h) Particle size distributions of pure perovskite
243 phosphor and NP-PP phosphor, respectively, after blending in silicone. The
244 ultrasonic power for all samples was 40 W. The matrix content for NP-PP
245 phosphors in films was 3.5 wt%. The phosphor concentration was 1.25 wt%.

246

247 In practice, the phosphor dispersity in packaging materials is much more
248 essential than that in non-packaging ones because it mainly determines the
249 application performance [43]. Herein, polydimethylsiloxane (PDMS) was selected
250 as the packaging material to obtain phosphor films with good mechanical
251 performance (**Fig. S12**). Photographs of the pure perovskite films and NP-PP
252 films under UV light irradiation are shown in **Fig. 4f**; the latter exhibits almost no
253 aggregation and a brighter green PL. To confirm the excellent dispersity of the
254 NP-PP phosphor, the particle size distributions of the pure perovskite and NP-PP
255 films were determined using confocal fluorescence images, as shown in **Fig. 4g**.
256 Our optimized NP-PP phosphor after packaging, still had a small mean size of 2.6
257 μm with a size deviation of 1 μm , which is two orders of magnitude lower than
258 that of the pure perovskite phosphor, which can be attributed to the
259 hydrophobicity of the NP-PP structure as observed from the increase in contact
260 angle from 0° to 130° (**Fig. S13**). Therefore, due to the hydrophobicity, the NP-PP

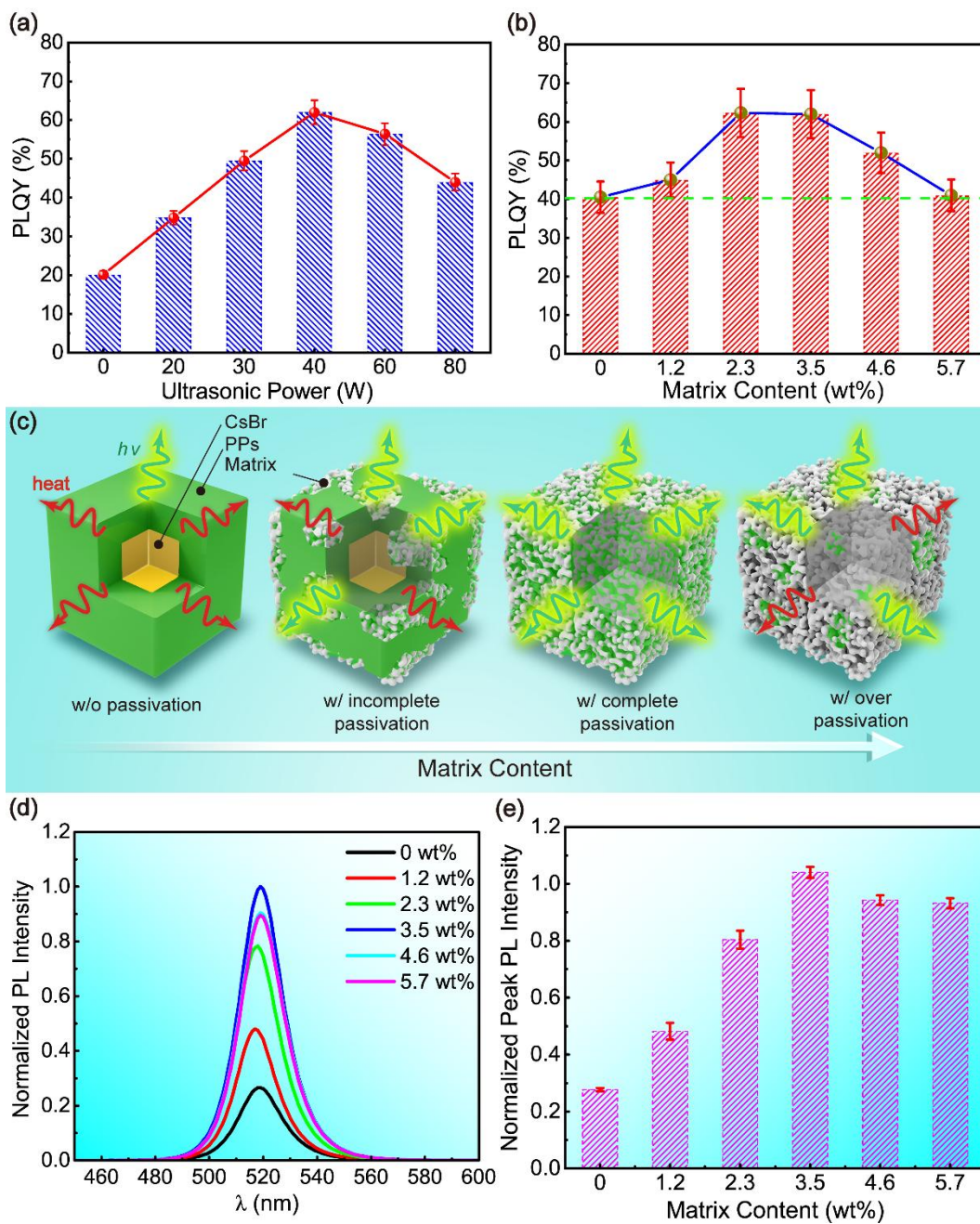
261 structure can also solve the aggregation issue as in previous studies, and the
262 boosted PEO efficiency will be determined by the IRS effect as discussed later.

263

264 *2.2.2 PLQY and PL intensity*

265 The PLQY measurement was used to characterize the PL performance of the NP-
266 PP phosphor before packaging, which is generally attributed to the crystal quality
267 [6, 37]. According to the morphology investigation, the PLQY values of the NP-
268 PP phosphor was also regulated by the ultrasonic power and matrix content, as
269 shown in **Fig. 5a-b**, respectively. As for the ultrasonic power regulation, the
270 PLQY reached a maximum value at the critical point of 40 W and then rolled off
271 with excess ultrasonic power. One reasonable explanation is that the enhanced
272 ultrasonic power mainly promotes the crystallization of the NP-PP phosphor
273 before the complete reaction. However, it may introduce surface defects on NP-
274 PPs because of the ultrasonic cavitation effect caused by excess reaction power,
275 leading to more trap-assisted recombination. This notion is further supported by
276 the increased slow-decay component a_2 in the PL decay measurement [44, 45], as
277 the ultrasonic power exceeded 40 W (**Fig. S14** and **Table S1**). As for the matrix
278 content regulation, the PLQY reached a maximum of 62% at the critical point of
279 ~3.5 wt% (optimized NP-PP phosphor), significantly increasing by 55%
280 compared with the pure perovskite phosphor without the matrix (PLQY of 40%).
281 These results demonstrated that the matrix well passivated the surface defects of
282 NP-PPs, which is consistent with previous reports using an SiO₂ shell as the

283 passivation layer for perovskites [46]. This notion is also supported by the longer
284 PL decay lifetime of the NP-PP phosphor as the matrix content increased to 3.5
285 wt% (**Fig. S15** and **Table S2**) because the aerogel matrix introduces other
286 recombination paths and led to a longer relaxation process. However, the PLQY
287 rolled off with excess matrix, with a high matrix content of 5.7 wt% leading to a
288 low PLQY. These results are further supported by the reduced PL decay lifetime
289 with an excess matrix content of 5.7 wt%; in other words, fast and non-radiative
290 recombination is introduced by an excess matrix content. The reason is that the
291 CsBr content in hybrid solid precursors is insufficient for constructing continuous
292 NP-PPs in the excess matrix, and a larger surface area is exposed without
293 passivation, resulting in many more surface defects (more non-radiative
294 recombination), as shown in **Fig. 5c**. Notably, achieving a high PLQY is out of
295 the scope of our study, which can be further improved by optimizing crystal
296 defects *via* ligand passivation in the future.



297

298 **Fig. 5. PL performance of NP-PP phosphor.** (a)-(b) PLQY of NP-PP phosphor

299 prepared at different ultrasonic powers (matrix content of 3.5 wt%) and matrix

300 contents (ultrasonic power of 40 W), respectively. (c) Diagram of NP-PP

301 phosphor with different matrix contents. (d) PL intensity and (e) peak PL intensity
302 of NP-PP films with different matrix contents. The ultrasonic power was 40 W,
303 and the phosphor concentration was 5 wt% for all samples.

304

305 In addition, the structure affects the light-matter interaction in the NP-PP
306 phosphor. Particularly, although the phosphor size shows no significant difference
307 as discussed in Section 2.2.1 (the aggregation difference is neglected), the
308 increased matrix content leads to a higher density of NP-PP structures in the
309 phosphor. The absorption and PL spectra of the NP-PP films (NP-PP phosphor
310 packaging in silicone) with different matrix contents are shown in **Fig. S16** and
311 **Fig. 5d**, respectively. The absorption spectra overlap with the PL spectrum around
312 520 nm due to the short Stoke's shift. The maximum PL intensity occurred at a
313 matrix content of 3.5 wt%, the same as that of PLQY. For convenience, the peak
314 PL intensity is shown in **Fig. 5e**. The peak PL intensity increased with the matrix
315 content before reaching 3.5 wt% then decreased, whose trend is similar to that of
316 PLQY. Interestingly, the optimized NP-PP films (matrix content of 3.5 wt%)
317 show a boosted peak PL intensity 2.8-fold higher than that of the pure perovskite
318 films. Therefore, the peak PL intensity largely benefited from the introduction of
319 the aerogel matrix, especially at low matrix contents. However, at high matrix
320 contents with a poor crystal quality as discussed above, the peak PL intensity only
321 slightly declines. These results imply that a strong light-matter interaction exists
322 in the perovskite phosphor with a denser NP-PP structure, which may originate

323 from the scattering effect of the aerogel matrix, as the haze of NP-PP films also
324 increased with the matrix content (**Fig. S17**). FDTD simulations were
325 subsequently carried out to investigate this issue and to confirm the PEO effect.

326

327 *2.3 IRS effect of NP-PP phosphor*

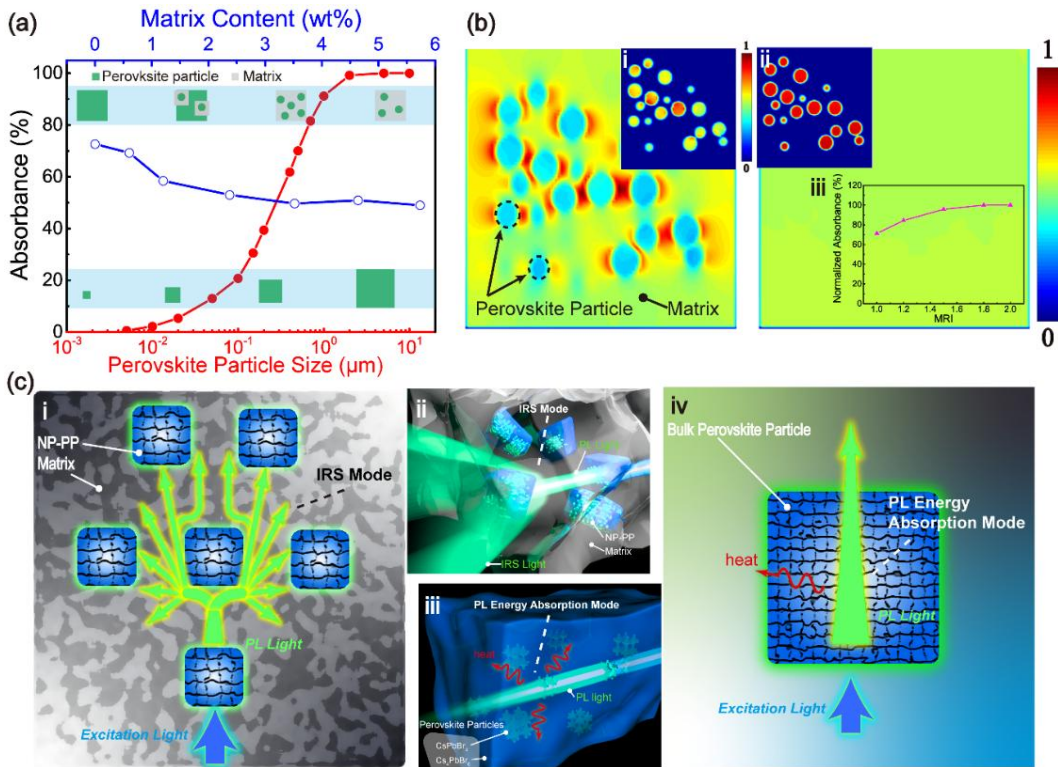
328 An FDTD simulation was performed to investigate the PL energy propagation of
329 the NP-PP phosphor, revealing its PEO mechanisms. The FDTD simulation
330 contained two cases: 1) PL energy propagating outward a DPP system, which
331 characterizes the internal PL energy absorption in a perovskite particle; 2) PL
332 energy propagating through a MPP system, which characterizes the overall PL
333 energy absorption among perovskite particles. For the DPP system, the perovskite
334 was assumed to be a cube, with its size varying from 5 nm to 10 μm (**Fig. S18**).
335 For the MPP system, non-overlapping perovskite particles were assumed to be
336 spherical uniformly and randomly distributed in a constant area, with their total
337 volume invariable when their size varied (5 - 100 nm). Lastly, based on the MPP
338 model, a NP-PP phosphor model was constructed, which was assumed to be an
339 SiO_2 cube (400 nm) with random non-overlapping nanopores occupied by NP-
340 PPs; the density and the size of NP-PPs were determined by the specific surface
341 area ($713 \text{ m}^2/\text{g}$), mean pore size (20 nm), and matrix content (from 0 to 6 wt%)
342 used in our cases. Because the perovskite phosphor and NP-PP phosphor were
343 mostly dominated by the Cs_4PbBr_6 component according to the XRD patterns, the
344 effective refractive index of the perovskite particles was defined as 1.8 [47]. It is

345 difficult to directly characterize the dynamic color conversion in the FDTD
346 method. Therefore, for the DPP system, a dipole source (520 nm) was located at
347 the center of the perovskite particle for modeling the internal PL energy
348 generation similar to previous reports [20, 22]. For the MPP system, a total-field
349 scattered-field (TFSF) source (520 nm) closely surrounded the system for
350 modeling the PL energy. The lower absorbance to the sources demonstrated better
351 PEO effect.

352

353 For the DPP system, the absorbance of the perovskite particle significantly
354 increased with a larger particle size, especially when the size reached the
355 submicron scale (~ 100 nm) (**Fig. 6a**). These results are attributed to the serious
356 absorption loss of PL energy inside the pure perovskite phosphor; a larger particle
357 size leads to a longer internal absorption path and higher optical loss, which is
358 consistent with previous reports [36, 48, 49]. Therefore, it is essential to control
359 the size of NP-PPs below submicron scale, which further support our selection of
360 aerogel with nanopores. As a result, we constructed a NP-PP structure in a
361 perovskite phosphor using aerogel matrix. For the NP-PP phosphor with a MPP
362 system, its absorbance with various matrix content is provided in **Fig. 6a**, the
363 refractive index of matrix (MRI) is 1.5. The absorbance of the NP-PP phosphor
364 decreases with the increased matrix content and well confirms the PEO
365 enhancement of NP-PP structure; the absorbance fluctuates slightly when the
366 matrix content over 3.5 wt%, which is consistent with the experimental results

367 achieving the maximum PL intensity.



368

369 **Fig. 6. PEO enhancement mechanism of NP-PP phosphor based on the IRS**

370 **effect of the NP-PP structure.** (a) Absorbance of the perovskite particle and NP-

371 PP phosphor with different sizes and matrix contents, respectively. (b) Total-field

372 and (i)-(ii) absorption-field energy flow density of the cross-sectional MPP system

373 with its MRI of 1.0 (left) and 2.0 (right). Two color bars are normalized with all

374 the total-field and absorption-field energy flow density, respectively. (iii) The

375 normalized absorbance curve of the MPP system with different MRIs. (c) (i) PEO

376 enhancement mechanisms through the IRS mode of the NP-PP structure compared

377 to (iv) the PL energy absorption mode of a bulk perovskite particle. (ii)-(iii) 3D

378 diagrams of (i) and (iv).

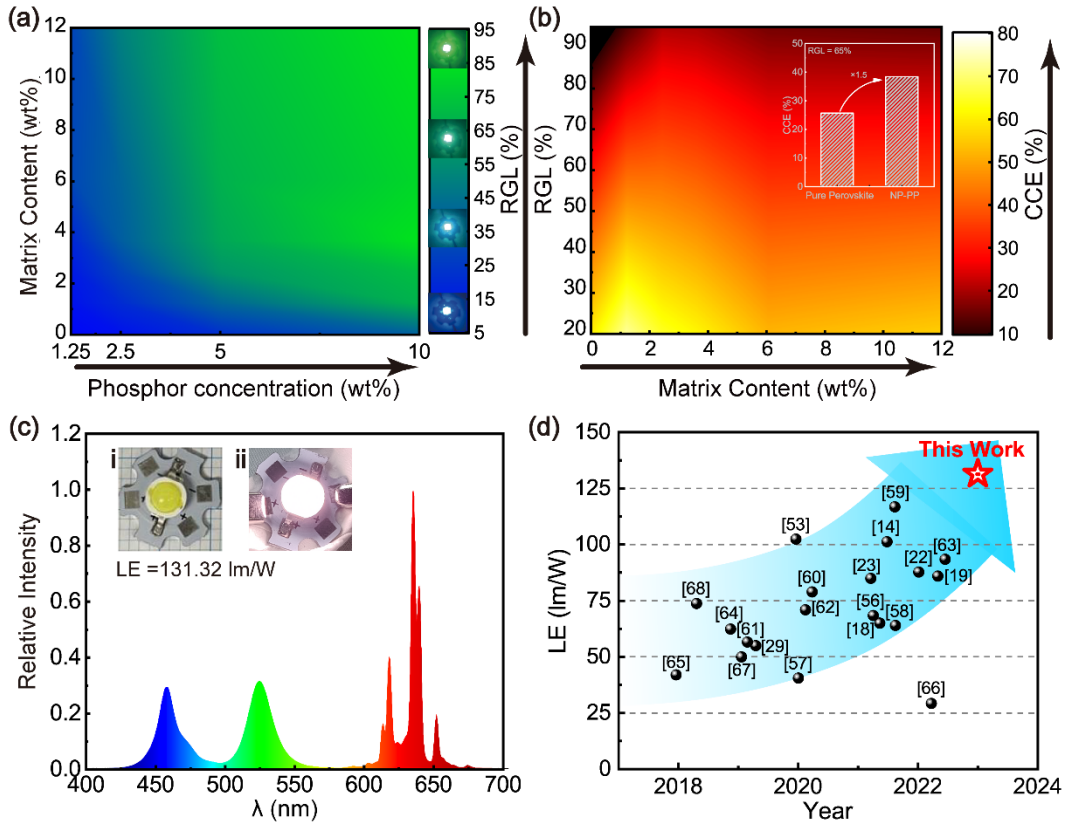
379

380 To have a deep understanding on the PEO enhancement, the energy flow
381 densities of NP-PP phosphor in a MPP system were investigated as shown in **Fig.**
382 **6b**, and the NP-PP phosphor without aerogel matrix (MRI = 1.8) was as a
383 reference. When the NP-PP phosphor had a low MRI, it was observed that the
384 total-field energy flow density was lower inside the perovskite particles but
385 dramatically higher near outside of the particle boundaries. One possibility is that
386 the high refractive NP-PPs serve as the internal resonant scatters [50] in the MPP
387 system, leading to the IRS effect. The strong scattering ability was further
388 confirmed by its larger scattering cross-section (**Fig. S19**). These results mean that
389 a portion of the PL energy is scattered when reaching NP-PPs, it tends to evade
390 NP-PPs and propagating into the matrix; in other words, the PL energy absorption
391 mode in NP-PPs transforms to the IRS mode in the matrix, as shown in **Fig. 6c**.
392 The lower absorption-field energy flow density of NP-PPs with lower MRI can
393 further support these results (**Fig. 6b-iii**), demonstrating the less PL energy
394 absorption of NP-PPs in the aerogel matrix. In addition, the above IRS effect was
395 also witnessed when changing the shape of NP-PPs (e.g., rectangle, ring, triangle)
396 (**Fig. S20**), indicating that the IRS effect exists in nanoparticles of general shapes.
397 Moreover, lower absorbance was obtained when a bulk perovskite particle (100
398 nm) was further divided into smaller particles, also supporting that the NP-PP
399 structure could effectively suppresses the internal PL energy absorption of a bulk
400 perovskite particle using the IRS effect (**Fig. S21**).

401

402 *2.4 White LED applications of NP-PP phosphor*

403 The NP-PP phosphor packaged in a blue LED chip confirmed the excellent
404 PEO performance. Generally, the CsPbBr₃ color converter is used to compensate
405 for the pure green spectra of LED devices, achieving white light for backlighting
406 or pure green light for active display [2, 6, 51]. A high ratio of green light (RGL)
407 from the color converter indicates excellent color tunability, particularly for
408 mini/micro LED active display devices [52], which is determined by the PL
409 intensity and can be obtained by increasing the phosphor concentration [53]. In
410 our cases, the RGL is defined by the intensity ratio of the green spectra (495-565
411 nm) to the whole spectrum as shown in **Fig. 7a**. The RGL is enhanced as the
412 phosphor concentration increases, which is consistent with previous reports [54].
413 However, the pure perovskite phosphor achieved an RGL below 40% even at a
414 high phosphor concentration of 10 wt%, appearing bluish in color (**Fig. S22**) on
415 the original LED chip, indicating its poor color tunability and low PL intensity.
416 Our NP-PP phosphor demonstrated a high RGL value because of its strong PL
417 enhancement. When compared at the same phosphor concentration of 10 wt%, the
418 RGL of the optimized NP-PP phosphor (matrix content of 3.5 wt%) exceeded
419 85%, which was approximately 2.2-fold that of the pure perovskite phosphor.
420 These results confirm the excellent color tunability of the NP-PP phosphor owing
421 to its strong PEO effect and high PL intensity.



422

423 **Fig. 7. Color conversion performance of NP-PP phosphor for LED devices.**

424 (a) RGL of NP-PP LEDs with different phosphor concentrations and matrix

425 contents. (b) Relationship between RGL and CCE of NP-PP LEDs with different

426 matrix contents. Inset: CCE comparison of pure perovskite and NP-PP when RGL

427 = 65%. (c) Spectrum and PEO efficiency of white LED device using NP-PP

428 phosphor as green converters. (i)-(ii) photograph of the white LED operated at 10

429 mA. (d) LE comparisons of white LEDs using halide perovskite as color

430 converters.

431

432 Although a high PL intensity helps to achieve good color tunability, it is also

433 accompanied by a low color-conversion efficiency (CCE) introduced by
434 conversion loss, especially the PL energy absorption loss mentioned above [55]. It
435 is essential to simultaneously obtain high CCE and RGL values when comparing
436 the PEO performance among different color converters [53]. Therefore, both the
437 CCE and RGL values are provided in **Fig. 7b** for comparing NP-PP phosphor
438 with different matrix contents. The CCE showed the same trend as the PLQY and
439 PL intensity discussed above, which increased with an increase in the matrix
440 content and then appeared as a roll-off. Additionally, the CCE value significantly
441 dropped at high RGL values of over 60%. For example, the CCE of pure
442 perovskite phosphor dropped to 14% when the RGL reached 80%. These results
443 are consistent with previous reports and attributed to severe PL energy absorption
444 loss at high phosphor concentrations [54]. However, our optimized NP-PP
445 phosphor (matrix content of 3.5 wt%) maintained high CCE values ranging from
446 30 to 40% corresponding to high RGL values, which was 50% higher than that of
447 the pure perovskite phosphor (when RGL = 65%). These results confirm that the
448 NP-PP structure is beneficial to improve the PEO efficiency of the perovskite
449 phosphor, simultaneously causing higher CCE and RGL values, compared to the
450 pure perovskite phosphor, which are two key factors for the real application of
451 color converters.

452

453 For comparison with reported studies, white LEDs combining green NP-PP
454 phosphor and commercial red KSF ($\text{K}_2\text{SiF}_6:\text{Mn}^{4+}$) phosphor were prepared as

455 shown in **Fig. 7c**. Our NP-PP phosphor exhibited an ultrahigh LE of 131.32 lm/W
456 according to the entrusted test recognized by the China National Accreditation
457 Service (**Fig. S23**); the corresponding color coordinates are (0.3335, 0.2987) and
458 the color gamut was 121% the value provided in National Television Standards
459 Committee (NTSC) standards (**Fig. S24**). Notably, the LE of our NP-PP phosphor
460 is higher than that in current reported white LEDs using green perovskite
461 phosphor (**Fig. 7d**) [14, 18, 19, 22, 23, 29, 53, 56-68]. Such a high enhancement
462 of NP-PP phosphor can be also confirmed by the referenced white LEDs using
463 pure perovskite phosphor (**Fig. S25**). These results confirm the excellent PEO
464 performance of NP-PP phosphor, which is caused by the well-designed NP-PP
465 structure as discussed above. Besides, our NP-PP phosphor preserved the
466 excellent working stability of the halide perovskite phosphor class (**Fig. S26**) [69,
467 70]. Slight (< 5%) PL attenuation was observed after being heated at 90 °C for 50
468 h. Consequently, our work provides essential insights into obtaining perovskite
469 phosphors that have evolved from highly efficient materials (high PLQY) to
470 highly efficient applications (high PEO) by utilizing the IRS effect in phosphor,
471 significantly accelerating the application in optoelectronic applications.

472

473 **3. Conclusions**

474 In this study, we utilized the IRS effect to boost the PEO of
475 CsPbBr₃/Cs₄PbBr₆ perovskite phosphor, which was realized by the NP-PP
476 structure *in-situ* synthesized in the phosphor. A NMHS-LI reaction was developed

477 to prepare the NP-PP phosphor, key parameters, i.e., ultrasonic power and matrix
478 content, were investigated to analyze the synthesis process. The optimized
479 phosphor with a denser NP-PP structure has excellent dispersity and enhanced PL
480 intensity, leading to the strong PEO (2.8-fold enhanced PL intensity) compared
481 with the pure perovskite phosphor. FDTD simulation results revealed that the NP-
482 PP structure can transform the PL energy absorption mode to the IRS mode, most
483 of the scattering PL energy evades NP-PPs instead of propagating inside, and thus
484 reducing the PL energy absorption loss. Finally, the optimized NP-PP phosphor
485 was applied to white LEDs, high RGL and CCE values can be simultaneously
486 obtained owing to the largely enhanced PL intensity extracting by the IRS effect,
487 thereby achieving ultrahigh LE of 131.32 lm/W based on green perovskite
488 phosphors. This study provides a general guide for efficient perovskite phosphors
489 utilizing the nano-porous matrix to enable the IRS effect, which greatly accelerate
490 the replacement of rare earth phosphor. Additionally, a detailed design of
491 nanopore structures of the matrix-based perovskite phosphor is essential to further
492 improve the PEO performance in future.

493

494 **4. Experimental section**

495 *Materials:* Cesium bromide (CsBr, 99.5%) and lead bromide (PbBr₂, 99%) were
496 purchased from Shanghai Macklin Biochemical Co., Ltd. Ethyl acetate (EA, 99%)
497 was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. N,N-
498 dimethylformamide (DMF, 99.5%) and n-hexane (C₆H₁₄, 97%) were purchased

499 from DAMAO Chemical Reagent Factory. Aerogel (SiO_2) was purchased from
500 Hengqiu Tech. Inc. Poly (dimethyl siloxane) (PDMS) was purchased from Dow
501 Corning. Red $\text{K}_2\text{SiF}_6:\text{Mn}^{4+}$ (KSF) phosphors were purchased from Shenzhen
502 Looking Long Technology Co., Ltd. Blue LED devices were purchased from
503 Foshan Nationstar Optoelectronics Company Ltd. All chemicals were used
504 directly without any further purification.

505

506 *Preparation of Cs-precursor:* CsBr (6 mmol) was dissolved in deionized water (5
507 mL) and aerogel (x mg, $x = 0, 20, 40, 60, 80, 100$, equivalent to the matrix content
508 of 0 wt%, 1.2 wt%, 2.3 wt%, 3.5 wt%, 4.6 wt% and 5.7 wt%, respectively) was
509 dispersed in ethanol (5 mL), which was assisted by stirring or ultrasonication. The
510 solution and dispersion liquids were then mixed and dried at 100 °C. The dried
511 solids were finally ground into powders.

512

513 *Synthesis of pure perovskite phosphor and NP-PP phosphor:* First, for the
514 synthesis of the pure perovskite phosphor, PbBr_2 (1 mmol) and CsBr (y mmol, $y =$
515 1, 2, 4, 6, 8, 10) were dissolved in DMF (10 mL); for the synthesis of NP-PP
516 phosphor, PbBr_2 (1 mmol) and Cs-precursor were dissolved in DMF (10 mL).
517 Second, the solution was placed in an ultrasonic crusher (BANDELIN, Electronic
518 GmbH) for the NMHS-LI reaction (p W, 5 min, 50 s ON, and 10 s OFF; $p = 0, 20,$
519 30, 40, 60, 80), whose probe was inserted below half the depth of the liquid level.
520 Third, the solution was transferred into a 20 mL centrifuge tube for centrifugation

521 (2000 rpm, 5 min). The supernatant was removed, and the precipitate was
522 dissolved in EA (10 ml) and centrifuged (2000 rpm, 5 min) for purification. Next,
523 the previous step was repeated, and the EA was replaced with n-hexane. Finally,
524 the precipitate was dried and ground into powders.

525

526 *Fabrication of pure perovskite and NP-PP films:* The as-prepared pure perovskite
527 phosphor or NP-PP phosphor (z mg, $z = 25, 51, 105, 222$, equivalent to the
528 phosphor concentration of 1.25 wt%, 2.5 wt%, 5 wt% and 10 wt%, respectively)
529 was uniformly mixed with polydimethylsiloxane (PDMS, 1.8 g) and a curing
530 agent (0.2 g) by vacuum defoaming for 5 min. Then, a flat square die (depth and
531 width of 1 mm and 4 mm, respectively) along with the mixture was dried at 90 °C
532 for 30 min to obtain a piece of pure perovskite or NP-PP film. After curing, the
533 film was removed from the die.

534

535 *Fabrication of white LED devices:* The as-prepared pure perovskite phosphor
536 (0.059 g) or NP-PP phosphor (0.020 g) was first grounded for minutes and then
537 uniformly mixed with commercial red KSF phosphor (0.115 g), PDMS (0.9 g),
538 and curing agent (0.1 g) by vacuum defoaming for 5 min. The mixture was later
539 injected into blue LED devices to finish the package. After curing at 60 °C for 2 h,
540 white LED devices were obtained.

541

542 *Characterization:* The morphology of the sample was characterized using

543 scanning electron microscope (SEM, Zeiss, Merlin) and high-resolution
544 transmission electron microscope (TEM, FEI, Talos F200X G2). The TEM slice
545 sample was obtained using focused ion beam scanning electron microscope (FIB-
546 SEM, FEI, Scios 2 HiVac). The phase and crystallography of the products were
547 characterized using an X-ray diffractometer (XRD, D/max3A, Bruker) at a
548 scanning rate of 10°/min in the 2 θ range from 10 to 80° using Cu K α radiation (λ
549 = 1.5418 Å). The corresponding EDS elemental mappings were captured on a
550 Bruker Nano GmbH Berlin instrument with a primary energy of 15 keV. The PL
551 spectra of the phosphors were recorded using a fluorescence spectrophotometer
552 (RF-6000, Shimadzu) with a Xe lamp as an excitation source, whose samples
553 were packaged in PDMS. The UV–vis absorption spectra and haze spectra of the
554 pure perovskite phosphor and NP-PP phosphor were recorded using a UV–vis
555 spectrometer (Shimadzu) in the wavelength range of 300–800 nm at 1 nm intervals.
556 Time-resolved fluorescence spectra were recorded using a steady-state
557 fluorescence spectrometer (FLS1000, Edinburgh). The PLQYs of the samples
558 (powder state before packaging) were measured using an absolute PLQY
559 spectrometer at an excitation wavelength of 365 nm (K.K. C9920, Hamamatsu
560 Photonics). The N₂ adsorption/desorption isotherms and pore size distributions of
561 the aerogel were obtained using a gas adsorption analyzer (TriStar II 3flex, Mike).
562 The contact angles of the aerogel were measured using a surface contact angle
563 tester (OCA40 Micro; Data Physics). The optical performances of the white LEDs
564 were measured by an integrating sphere system (Instrument Systems), and the

565 injection current was provided by a power source (Keithley). All reliability tests
566 were conducted under laboratory conditions at a constant ambient temperature of
567 25 °C.

568

569 **Acknowledgements**

570 The authors acknowledge financial support from Science & Technology Program
571 of Guangdong Province (2020B0101030008, 2020B121202003), Natural Science
572 Foundation of Guangdong Province (2022A1515011059), China Postdoctoral
573 Science Foundation (2020M680122, 2022M710697).

574

575 **Appendix A. Supplementary information**

576 Supplementary information associated with this article can be found in the online
577 version.

578

579 **References**

- 580 [1] Q. Chen, J. Wu, X. Ou, B. Huang, J. Almutlaq, A.A. Zhumekenov, X. Guan, S. Han, L. Liang,
581 Z. Yi, J. Li, X. Xie, Y. Wang, Y. Li, D. Fan, D.B.L. Teh, A.H. All, O.F. Mohammed, O.M.
582 Bakr, T. Wu, M. Bettinelli, H. Yang, W. Huang, X. Liu, All-inorganic perovskite
583 nanocrystal scintillators, *Nature* 561(7721) (2018) 88-93. [https://doi.org/10.1038/s41586-](https://doi.org/10.1038/s41586-018-0451-1)
584 018-0451-1.
- 585 [2] K. Lin, J. Xing, L.N. Quan, F.P.G. de Arquer, X. Gong, J. Lu, L. Xie, W. Zhao, D. Zhang, C.
586 Yan, W. Li, X. Liu, Y. Lu, J. Kirman, E.H. Sargent, Q. Xiong, Z. Wei, Perovskite light-
587 emitting diodes with external quantum efficiency exceeding 20 per cent, *Nature* 562(7726)

- 588 (2018) 245-248. <https://doi.org/10.1038/s41586-018-0575-3>.
- 589 [3] Y. Chen, Y. Lei, Y. Li, Y. Yu, J. Cai, M.-H. Chiu, R. Rao, Y. Gu, C. Wang, W. Choi, H. Hu,
590 C. Wang, Y. Li, J. Song, J. Zhang, B. Qi, M. Lin, Z. Zhang, A.E. Islam, B. Maruyama, S.
591 Dayeh, L.-J. Li, K. Yang, Y.-H. Lo, S. Xu, Strain engineering and epitaxial stabilization of
592 halide perovskites, *Nature* 577(7789) (2020) 209-215. [https://doi.org/10.1038/s41586-019-](https://doi.org/10.1038/s41586-019-1868-x)
593 1868-x.
- 594 [4] C. Qin, A.S.D. Sandanayaka, C. Zhao, T. Matsushima, D. Zhang, T. Fujihara, C. Adachi,
595 Stable room-temperature continuous-wave lasing in quasi-2D perovskite films, *Nature*
596 585(7823) (2020) 53-57. <https://doi.org/10.1038/s41586-020-2621-1>.
- 597 [5] C. Chen, S. Zheng, H. Song, Photon management to reduce energy loss in perovskite solar
598 cells, *Chemical Society Reviews* 50(12) (2021) 7250-7329.
599 <https://doi.org/10.1039/d0cs01488e>.
- 600 [6] X.-K. Liu, W. Xu, S. Bai, Y. Jin, J. Wang, R.H. Friend, F. Gao, Metal halide perovskites for
601 light-emitting diodes, *Nature Materials* 20(1) (2021) 10-21. [https://doi.org/10.1038/s41563-](https://doi.org/10.1038/s41563-020-0784-7)
602 020-0784-7.
- 603 [7] S. Tan, T. Huang, I. Yavuz, R. Wang, T.W. Yoon, M. Xu, Q. Xing, K. Park, D.-K. Lee, C.-H.
604 Chen, R. Zheng, T. Yoon, Y. Zhao, H.-C. Wang, D. Meng, J. Xue, Y.J. Song, X. Pan, N.-G.
605 Park, J.-W. Lee, Y. Yang, Stability-limiting heterointerfaces of perovskite photovoltaics,
606 *Nature* (2022). <https://doi.org/10.1038/s41586-022-04604-5>.
- 607 [8] L. Protesescu, S. Yakunin, M.I. Bodnarchuk, F. Krieg, R. Caputo, C.H. Hendon, R.X. Yang, A.
608 Walsh, M.V. Kovalenko, Nanocrystals of Cesium Lead Halide Perovskites (CsPbX₃, X = Cl,
609 Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color
610 Gamut, *Nano Letters* 15(6) (2015) 3692-3696. <https://doi.org/10.1021/nl5048779>.
- 611 [9] D.D. Yang, X.M. Li, W.H. Zhou, S.L. Zhang, C.F. Meng, Y. Wu, Y. Wang, H.B. Zeng,
612 CsPbBr₃ Quantum Dots 2.0: Benzenesulfonic Acid Equivalent Ligand Awakens Complete
613 Purification, *Advanced Materials* 31(30) (2019). <https://doi.org/10.1002/adma.201900767>.

- 614 [10] C.H. Lu, G.V. Biesold, Y.J. Liu, Z.T. Kang, Z.Q. Lin, Doping and ion substitution in
615 colloidal metal halide perovskite nanocrystals, *Chemical Society Reviews* 49(14) (2020)
616 4953-5007. <https://doi.org/10.1039/c9cs00790c>.
- 617 [11] I. Moreels, Y. Justo, B. De Geyter, K. Haustraete, J.C. Martins, Z. Hens, Size-Tunable,
618 Bright, and Stable PbS Quantum Dots: A Surface Chemistry Study, *ACS Nano* 5(3) (2011)
619 2004-2012. <https://doi.org/10.1021/nn103050w>.
- 620 [12] L.H. Qu, X.G. Peng, Control of photoluminescence properties of CdSe nanocrystals in
621 growth, *Journal of the American Chemical Society* 124(9) (2002) 2049-2055.
622 <https://doi.org/10.1021/ja017002j>.
- 623 [13] X.G. Wu, H. Ji, X. Yan, H. Zhong, Industry outlook of perovskite quantum dots for display
624 applications, *Nature Nanotechnology* (2022). <https://doi.org/10.1038/s41565-022-01163-8>.
- 625 [14] K. Du, L. He, S. Song, J. Feng, Y. Li, M. Zhang, H. Li, C. Li, H. Zhang, In Situ Embedding
626 Synthesis of Highly Stable CsPbBr₃/CsPb₂Br₅@PbBr(OH) Nano/Microspheres through
627 Water Assisted Strategy, *Advanced Functional Materials* 31(36) (2021).
628 <https://doi.org/10.1002/adfm.202103275>.
- 629 [15] K.Y. Baek, W. Lee, J. Lee, J. Kim, H. Ahn, J.I. Kim, J. Kim, H. Lim, J. Shin, Y.J. Ko, H.D.
630 Lee, R.H. Friend, T.W. Lee, J. Lee, K. Kang, T. Lee, Mechanochemistry-driven engineering
631 of 0D/3D heterostructure for designing highly luminescent Cs-Pb-Br perovskites, *Nat*
632 *Commun* 13(1) (2022) 4263. <https://doi.org/10.1038/s41467-022-31924-x>.
- 633 [16] H.W. Lian, Y. Li, K. Sharafudeen, W.R. Zhao, G.R. Krishnan, S.A. Zhang, J.R. Qiu, K.
634 Huang, G. Han, Highly Thermotolerant Metal Halide Perovskite Solids, *Advanced Materials*
635 32(28) (2020). <https://doi.org/10.1002/adma.202002495>.
- 636 [17] DOE BTO Solid-State Lighting Program, 2022 DOE SSL R&D Opportunities, 2022.
637 <https://www.energy.gov/sites/default/files/2022-02/2022-ssl-rd-opportunities.pdf>. (Accessed
638 2 February 2022).
- 639 [18] Y.Y. Duan, G.Z. Yin, D.Y. Wang, R.D. Costa, In Situ Ambient Preparation of Perovskite-

640 Poly(L-lactic acid) Phosphors for Highly Stable and Efficient Hybrid Light-Emitting Diodes,
641 ACS Applied Materials & Interfaces 13(18) (2021) 21800-21809.
642 <https://doi.org/10.1021/acsami.1c04025>.

643 [19] T.T. Xuan, S.Q. Guo, W.H. Bai, T.L. Zhou, L. Wang, R.J. Xie, Ultrastable and highly
644 efficient green-emitting perovskite quantum dot composites for Mini-LED displays or
645 backlights, Nano Energy 95 (2022). <https://doi.org/10.1016/j.nanoen.2022.107003>.

646 [20] J.S. Li, Y. Tang, Z.T. Li, J.X. Li, X.R. Ding, B.H. Yu, S.D. Yu, J.Z. Ou, H.C. Kuo, Toward
647 200 Lumens per Watt of Quantum-Dot White-Light-Emitting Diodes by Reducing
648 Reabsorption Loss, ACS Nano 15(1) (2021) 550-562.
649 <https://doi.org/10.1021/acsnano.0c05735>.

650 [21] A. Fakharuddin, M.K. Gangishetty, M. Abdi-Jalebi, S.H. Chin, A.B. Yusoff, D.N. Congreve,
651 W. Tress, F. Deschler, M. Vasilopoulou, H.J. Bolink, Perovskite light-emitting diodes, Nature
652 Electronics 5(4) (2022) 203-216. <https://doi.org/10.1038/s41928-022-00745-7>.

653 [22] J.J. Ren, A. Meijerink, X.P. Zhou, J.P. Wu, G.Y. Zhang, Y.H. Wang, In Situ Embedding
654 Synthesis of CsPbBr₃@Ce-MOF@SiO₂ Nanocomposites for High Efficiency Light-Emitting
655 Diodes: Suppressing Reabsorption Losses through the Waveguiding Effect, ACS Applied
656 Materials & Interfaces 14(2) (2022) 3176-3188. <https://doi.org/10.1021/acsami.1c20804>.

657 [23] Q. Zhang, W. Zheng, Q. Wan, M. Liu, X. Feng, L. Kong, L. Li, Confined Synthesis of Stable
658 and Uniform CsPbBr₃ Nanocrystals with High Quantum Yield up to 90% by High
659 Temperature Solid - State Reaction, Advanced Optical Materials 9(11) (2021).
660 <https://doi.org/10.1002/adom.202002130>.

661 [24] J. Chen, S. Mukherjee, W. Li, H. Zeng, R.A. Fischer, Bespoke crystalline hybrids towards the
662 next generation of white LEDs, Nature Reviews Materials (2022).
663 <https://doi.org/10.1038/s41578-022-00476-3>.

664 [25] K.M. McCall, K. Sakhatskyi, E. Lehmann, B. Walfort, A.S. Losko, F. Montanarella, M.I.
665 Bodnarchuk, F. Krieg, Y. Kelestemur, D. Mannes, Y. Shynkarenko, S. Yakunin, M.V.

666 Kovalenko, Fast Neutron Imaging with Semiconductor Nanocrystal Scintillators, *ACS Nano*
667 14(11) (2020) 14686-14697. <https://doi.org/10.1021/acsnano.0c06381>.

668 [26] L.N. Quan, R. Quintero-Bermudez, O. Voznyy, G. Walters, A. Jain, J.Z. Fan, X.L. Zheng,
669 Z.Y. Yang, E.H. Sargent, Highly Emissive Green Perovskite Nanocrystals in a Solid State
670 Crystalline Matrix, *Advanced Materials* 29(21) (2017) 6.
671 <https://doi.org/10.1002/adma.201605945>.

672 [27] T. Jin, Z. Liu, J. Luo, J.-H. Yuan, H. Wang, Z. Xie, W. Pan, H. Wu, K.-H. Xue, L. Liu, Z. Hu,
673 Z. Zheng, J. Tang, G. Niu, Self-wavelength shifting in two-dimensional perovskite for
674 sensitive and fast gamma-ray detection, *Nature Communications* 14(1) (2023).
675 <https://doi.org/10.1038/s41467-023-38545-y>.

676 [28] C.Y. Kong, C.H. Lin, C.H. Lin, T.Y. Li, S.W.H. Chen, C.L. Tsai, C.W. Sher, T.Z. Wu, P.T.
677 Lee, X.Z. Xu, M.L. Zhang, C.H. Ho, J.H. He, H.C. Kuo, Highly Efficient and Stable White
678 Light-Emitting Diodes Using Perovskite Quantum Dot Paper, *Advanced Science* 6(24)
679 (2019). <https://doi.org/10.1002/advs.201902230>.

680 [29] T.T. Xuan, J.J. Huang, H. Liu, S.Q. Lou, L.Y. Cao, W.J. Gan, R.S. Liu, J. Wang, Super-
681 Hydrophobic Cesium Lead Halide Perovskite Quantum Dot-Polymer Composites with High
682 Stability and Luminescent Efficiency for Wide Color Gamut White Light-Emitting Diodes,
683 *Chemistry of Materials* 31(3) (2019) 1042-1047.
684 <https://doi.org/10.1021/acs.chemmater.8b04596>.

685 [30] J. Hao, Z. Dai, M. Guan, P. Dang, H. Wang, C. Yan, J. Lin, G. Li, Simultaneous enhancement
686 of luminescence and stability of lead halide perovskites by a diatomite microcavity for light-
687 emitting diodes, *Chemical Engineering Journal* 417 (2021).
688 <https://doi.org/10.1016/j.cej.2020.128056>.

689 [31] W.Q. Yang, F. Gao, Y. Qiu, W.Z. Liu, H.Y. Xu, L.L. Yang, Y.C. Liu, CsPbBr₃-Quantum-
690 Dots/Polystyrene@Silica Hybrid Microsphere Structures with Significantly Improved
691 Stability for White LEDs, *Advanced Optical Materials* 7(13) (2019).

- 692 <https://doi.org/10.1002/adom.201900546>.
- 693 [32] H.C. Wang, S.Y. Lin, A.C. Tang, B.P. Singh, H.C. Tong, C.Y. Chen, Y.C. Lee, T.L. Tsai,
694 R.S. Liu, Mesoporous Silica Particles Integrated with All-Inorganic CsPbBr₃ Perovskite
695 Quantum-Dot Nanocomposites (MP-PQDs) with High Stability and Wide Color Gamut Used
696 for Backlight Display, *Angewandte Chemie International Edition* 55(28) (2016) 7924-7929.
697 <https://doi.org/10.1002/anie.201603698>.
- 698 [33] C. Sun, Y. Zhang, C. Ruan, C.Y. Yin, X.Y. Wang, Y.D. Wang, W.W. Yu, Efficient and
699 Stable White LEDs with Silica-Coated Inorganic Perovskite Quantum Dots, *Advanced*
700 *Materials* 28(45) (2016) 10088-10094. <https://doi.org/10.1002/adma.201603081>.
- 701 [34] J.W. Hou, P. Chen, A. Shukla, A. Krajnc, T.S. Wang, X.M. Li, R. Doasa, L.H.G. Tizei, B.
702 Chan, D.N. Johnstone, R.J. Lin, T.U. Schulli, I. Martens, D. Appadoo, M.S. Ari, Z.L. Wang,
703 T. Wei, S.C. Lo, M.Y. Lu, S.C. Li, E.B. Namdas, G. Mali, A.K. Cheetham, S.M. Collins, V.
704 Chen, L.Z. Wang, T.D. Bennett, Liquid-phase sintering of lead halide perovskites and metal-
705 organic framework glasses, *Science* 374(6567) (2021) 621-625.
706 <https://doi.org/10.1126/science.abf4460>.
- 707 [35] Y. He, Y.J. Yoon, Y.W. Harn, G.V. Biesold-McGee, S. Liang, C.H. Lin, V.V. Tsukruk, N.
708 Thadhani, Z.T. Kang, Z.Q. Lin, Unconventional route to dual-shelled organolead halide
709 perovskite nanocrystals with controlled dimensions, surface chemistry, and stabilities,
710 *Science Advances* 5(11) (2019). <https://doi.org/10.1126/sciadv.aax4424>.
- 711 [36] B. Mendewala, E.T. Vickers, K. Nikolaidou, A. DiBenedetto, W.G. Delmas, J.Z. Zhang, S.
712 Ghosh, High Efficiency Luminescent Solar Concentrator based on Organo - Metal Halide
713 Perovskite Quantum Dots with Plasmon Enhancement, *Advanced Optical Materials* 9(20)
714 (2021). <https://doi.org/10.1002/adom.202100754>.
- 715 [37] C.H. Bi, Z.W. Yao, X.J. Sun, X.C. Wei, J.X. Wang, J.J. Tian, Perovskite Quantum Dots with
716 Ultralow Trap Density by Acid Etching-Driven Ligand Exchange for High Luminance and
717 Stable Pure-Blue Light-Emitting Diodes, *Advanced Materials* 33(15) (2021).

- 718 <https://doi.org/10.1002/adma.202006722>.
- 719 [38] J.Z. Song, J.H. Li, L.M. Xu, J.H. Li, F.J. Zhang, B.N. Han, Q.S. Shan, H.B. Zeng, Room-
720 Temperature Triple-Ligand Surface Engineering Synergistically Boosts Ink Stability,
721 Recombination Dynamics, and Charge Injection toward EQE-11.6% Perovskite QLEDs,
722 *Advanced Materials* 30(30) (2018). <https://doi.org/10.1002/adma.201800764>.
- 723 [39] Z. Li, C. Song, J. Li, G. Liang, L. Rao, S. Yu, X. Ding, Y. Tang, B. Yu, J. Ou, U. Lemmer, G.
724 Gomard, Highly Efficient and Water - Stable Lead Halide Perovskite Quantum Dots Using
725 Superhydrophobic Aerogel Inorganic Matrix for White Light - Emitting Diodes, *Advanced*
726 *Materials Technologies* 5(2) (2020). <https://doi.org/10.1002/admt.201900941>.
- 727 [40] R. Cheng, Z.B. Liang, L. Zhu, H. Li, Y. Zhang, C.F. Wang, S. Chen, Fibrous Nanoreactors
728 from Microfluidic Blow Spinning for Mass Production of Highly Stable Ligand-Free
729 Perovskite Quantum Dots, *Angew Chem Int Ed Engl* 61(27) (2022) e202204371.
730 <https://doi.org/10.1002/anie.202204371>.
- 731 [41] Z. Dong, D. Fernandez Rivas, S. Kuhn, Acoustophoretic focusing effects on particle synthesis
732 and clogging in microreactors, *Lab Chip* 19(2) (2019) 316-327.
733 <https://doi.org/10.1039/c8lc00675j>.
- 734 [42] M. Li, Z. Liu, W. Yao, C. Xu, Y. Yu, M. Yang, G. Chen, Ultrasonic cavitation-enabled
735 microfluidic approach toward the continuous synthesis of cesium lead halide perovskite
736 nanocrystals, *Chinese Journal of Chemical Engineering* 59 (2023) 32-41.
737 <https://doi.org/10.1016/j.cjche.2022.12.001>.
- 738 [43] G.G. Li, Y. Tian, Y. Zhao, J. Lin, Recent progress in luminescence tuning of Ce³⁺ and Eu²⁺-
739 activated phosphors for pc-WLEDs, *Chemical Society Reviews* 44(23) (2015) 8688-8713.
740 <https://doi.org/10.1039/c4cs00446a>.
- 741 [44] W. Ding, H. Liu, S. Zhang, D. Qiu, X. Li, S. Wang, Transformation of Quasi - 2D Perovskite
742 into 3D Perovskite Using Formamidinium Acetate Additive for Efficient Blue Light - Emitting

- 743 Diodes, *Advanced Functional Materials* 32(8) (2021).
744 <https://doi.org/10.1002/adfm.202105164>.
- 745 [45] L. Zhao, J. Gao, Y.L. Lin, Y.W. Yeh, K.M. Lee, N. Yao, Y.L. Loo, B.P. Rand, Electrical
746 Stress Influences the Efficiency of CH₃NH₃PbI₃ Perovskite Light Emitting Devices,
747 *Advanced Materials* 29(24) (2017). <https://doi.org/10.1002/adma.201605317>.
- 748 [46] Q.X. Zhong, M.H. Cao, H.C. Hu, D. Yang, M. Chen, P.L. Li, L.Z. Wu, Q. Zhang, One-Pot
749 Synthesis of Highly Stable CsPbBr₃@SiO₂ Core-Shell Nanoparticles, *ACS Nano* 12(8)
750 (2018) 8579-8587. <https://doi.org/10.1021/acsnano.8b04209>.
- 751 [47] L. Zhang, S. Lin, Dimensional tailoring of halide perovskite: A case study on
752 Cs₄PbBr₆/CsPbBr₃ hybrid with molecular halide perovskite, *Solar Energy Materials and*
753 *Solar Cells* 204 (2020). <https://doi.org/10.1016/j.solmat.2019.110237>.
- 754 [48] H. Li, K. Wu, J. Lim, H.-J. Song, V.I. Klimov, Doctor-blade deposition of quantum dots onto
755 standard window glass for low-loss large-area luminescent solar concentrators, *Nature Energy*
756 1(12) (2016). <https://doi.org/10.1038/nenergy.2016.157>.
- 757 [49] B. Mendewala, K. Nikolaidou, C. Hoffman, S. Sarang, J. Lu, B. Ilan, S. Ghosh, The potential
758 of scalability in high efficiency hybrid perovskite thin film luminescent solar concentrators,
759 *Solar Energy* 183 (2019) 392-397. <https://doi.org/10.1016/j.solener.2019.03.042>.
- 760 [50] Z.P. Hu, Z.Z. Liu, Y. Bian, S.Q. Li, X.S. Tang, J. Du, Z.G. Zang, M. Zhou, W. Hu, Y.X.
761 Tian, Y.X. Leng, Enhanced Two-Photon-Pumped Emission from In Situ Synthesized
762 Nonblinking CsPbBr₃/SiO₂ Nanocrystals with Excellent Stability, *Advanced Optical*
763 *Materials* 6(3) (2018). <https://doi.org/10.1002/adom.201700997>.
- 764 [51] M.L. Zhang, Y. Li, K.M. Du, X. Gao, Y. Lu, D. Wen, S. Yao, J. Feng, H.J. Zhang, One-step
765 conversion of CsPbBr₃ into Cs₄PbBr₆/CsPbBr₃@Ta₂O₅ core-shell microcrystals with
766 enhanced stability and photoluminescence, *Journal of Materials Chemistry C* 9(4) (2021)
767 1228-1234. <https://doi.org/10.1039/d0tc05039c>.
- 768 [52] Y.G. Huang, E.L. Hsiang, M.Y. Deng, S.T. Wu, Mini-LED, Micro-LED and OLED displays:

- 769 present status and future perspectives, *Light: Science & Applications* 9(1) (2020).
770 <https://doi.org/10.1038/s41377-020-0341-9>.
- 771 [53] Z.L. Zhang, L.L. Shen, H.L. Zhang, L. Ding, G.Z. Shao, X.J. Liang, W.D. Xiang, Novel red-
772 emitting CsPb_{1-x}Ti_xI₃ perovskite QDs@glasses with ambient stability for high efficiency
773 white LEDs and plant growth LEDs, *Chemical Engineering Journal* 378 (2019).
774 <https://doi.org/10.1016/j.cej.2019.122125>.
- 775 [54] M. He, W. Chunyun, J.Z. Li, J.W. Wu, S. Zhang, H.C. Kuo, L.Y. Shao, S.C. Zhao, J.Z.
776 Zhang, F.Y. Kang, G.D. Wei, CsPbBr₃-Cs₄PbBr₆ composite nanocrystals for highly efficient
777 pure green light emission, *Nanoscale* 11(47) (2019) 22899-22906.
778 <https://doi.org/10.1039/c9nr07096f>.
- 779 [55] Z.C. Li, L. Kong, S.Q. Huang, L. Li, Highly Luminescent and Ultrastable CsPbBr₃
780 Perovskite Quantum Dots Incorporated into a Silica/Alumina Monolith, *Angewandte Chemie*
781 *International Edition* 56(28) (2017) 8134-8138. <https://doi.org/10.1002/anie.201703264>.
- 782 [56] X.S. Tang, W.W. Chen, Z.Z. Liu, J. Du, Z.Q. Yao, Y. Huang, C. Chen, Z.Q. Yang, T.C. Shi,
783 W. Hu, Z.G. Zang, Y. Chen, Y.X. Leng, Ultrathin, Core-Shell Structured SiO₂ Coated Mn²⁺-
784 Doped Perovskite Quantum Dots for Bright White Light-Emitting Diodes, *Small* 15(19)
785 (2019). <https://doi.org/10.1002/sml.201900484>.
- 786 [57] H.L. Guan, S.Y. Zhao, H.X. Wang, D.D. Yan, M. Wang, Z.G. Zang, Room temperature
787 synthesis of stable single silica-coated CsPbBr₃ quantum dots combining tunable red
788 emission of Ag-In-Zn-S for High-CRI white light-emitting diodes, *Nano Energy* 67 (2020).
789 <https://doi.org/10.1016/j.nanoen.2019.104279>.
- 790 [58] Q.H. Mo, C. Chen, W.S. Cai, S.Y. Zhao, D.D. Yan, Z.G. Zang, Room Temperature Synthesis
791 of Stable Zirconia-Coated CsPbBr₃ Nanocrystals for White Light-Emitting Diodes and
792 Visible Light Communication, *Laser & Photonics Reviews* 15(10) (2021).
793 <https://doi.org/10.1002/lpor.202100278>.
- 794 [59] Y. Li, K.M. Du, M.L. Zhang, X. Gao, Y. Lu, S. Yao, C.Y. Li, J. Feng, H.J. Zhang, Tunable

795 ultra-uniform Cs₄PbBr₆ perovskites with efficient photoluminescence and excellent stability
796 for high-performance white light-emitting diodes, *Journal of Materials Chemistry C* 9(37)
797 (2021) 12811-12818. <https://doi.org/10.1039/d1tc02210e>.

798 [60] F. Zheng, B.B. Yang, P.Y. Cao, X.L. Qian, J. Zou, A novel bulk phosphor for white LEDs:
799 CsPbBr₃/Cs₄PbBr₆ composite quantum dots-embedded borosilicate glass with high PLQY
800 and excellent stability, *Journal of Alloys and Compounds* 818 (2020).
801 <https://doi.org/10.1016/j.jallcom.2019.153307>.

802 [61] H.G. Wu, S. Wang, F. Cao, J.P. Zhou, Q.Q. Wu, H.R. Wang, X.M. Li, L.Q. Yin, X.Y. Yang,
803 Ultrastable Inorganic Perovskite Nanocrystals Coated with a Thick Long-Chain Polymer for
804 Efficient White Light-Emitting Diodes, *Chemistry of Materials* 31(6) (2019) 1936-1940.
805 <https://doi.org/10.1021/acs.chemmater.8b04634>.

806 [62] Y.X. Liu, D. Li, L.L. Zhang, Y.J. Chen, C. Geng, S.S. Shi, Z.Z. Zhang, W.G. Bi, S. Xu,
807 Amine- and Acid-Free Synthesis of Stable CsPbBr₃ Perovskite Nanocrystals, *Chemistry of*
808 *Materials* 32(5) (2020) 1904-1913. <https://doi.org/10.1021/acs.chemmater.9b04558>.

809 [63] Y. Zhang, G.S. Li, G.N. Hou, J.Q. Lin, M.S. Chen, S.H. Liu, H.C. Lin, J.F. Fang, C.B. Jing,
810 J.H. Chu, Multidentate ligand passivation enabled enhanced photoluminescence and stability
811 of CsPbBr₃ nanocrystals for white light-emitting diodes, *Chemical Engineering Journal* 438
812 (2022). <https://doi.org/10.1016/j.cej.2022.135270>.

813 [64] Y.H. Song, S.Y. Park, J.S. Yoo, W.K. Park, H.S. Kim, S.H. Choi, S. Bin Kwon, B.K. Kang,
814 J.P. Kim, H.S. Jung, D.H. Yoon, W.S. Yang, Y.S. Seo, Efficient and stable green-emitting
815 CsPbBr₃ perovskite nanocrystals in a microcapsule for light emitting diodes, *Chemical*
816 *Engineering Journal* 352 (2018) 957-963. <https://doi.org/10.1016/j.cej.2018.05.153>.

817 [65] S.J. Liu, M.L. He, X.X. Di, P.Z. Li, W.D. Xiang, X.J. Liang, CsPbX₃ nanocrystals films
818 coated on YAG:Ce³⁺ PiG for warm white lighting source, *Chemical Engineering Journal* 330
819 (2017) 823-830. <https://doi.org/10.1016/j.cej.2017.08.032>.

820 [66] C. Zhao, Y.K. Li, W.G. Ye, X.F. Shen, Z.C. Wen, X.Y. Yuan, Y.G. Cao, C.Y. Ma, Ligand-

821 Free CsPbBr₃ Perovskite Quantum Dots in Silica-Aerogel Composites with Enhanced
822 Stability for w-LED and Display by Substituting Pb²⁺ with Pr³⁺ or Gd³⁺ Ions, *Advanced*
823 *Optical Materials* 10(10) (2022). <https://doi.org/10.1002/adom.202102200>.

824 [67] H.Y. Liu, Y.S. Tan, M.H. Cao, H.C. Hu, L.Z. Wu, X.Y. Yu, L. Wang, B.Q. Sun, Q. Zhang,
825 Fabricating CsPbX₃-Based Type I and Type II Heterostructures by Tuning the Halide
826 Composition of Janus CsPbX₃/ZrO₂ Nanocrystals, *ACS Nano* 13(5) (2019) 5366-5374.
827 <https://doi.org/10.1021/acsnano.9b00001>.

828 [68] Y.M. Chen, Y. Zhou, Q. Zhao, J.Y. Zhang, J.P. Ma, T.T. Xuan, S.Q. Guo, Z.J. Yong, J.
829 Wang, Y. Kuroiwa, C. Moriyoshi, H.T. Sun, Cs₄PbBr₆/CsPbBr₃ Perovskite Composites with
830 Near-Unity Luminescence Quantum Yield: Large-Scale Synthesis, Luminescence and
831 Formation Mechanism, and White Light-Emitting Diode Application, *ACS Applied Materials*
832 *& Interfaces* 10(18) (2018) 15905-15912. <https://doi.org/10.1021/acscami.8b04556>.

833 [69] Y.S. Tan, R.Y. Li, H. Xu, Y.S. Qin, T. Song, B.Q. Sun, Ultrastable and Reversible
834 Fluorescent Perovskite Films Used for Flexible Instantaneous Display, *Advanced Functional*
835 *Materials* 29(23) (2019). <https://doi.org/10.1002/adfm.201900730>.

836 [70] C. Fan, H. Liu, J. Zhou, X. Dai, H. He, Z. Ye, Ultrastable and highly efficient CsPbBr₃
837 composites achieved by dual-matrix encapsulation for display devices, *Infomat* (2023).
838 <https://doi.org/10.1002/inf2.12417>.

839