Research Article

Air-Resistant Lead Halide Perovskite Nanocrystals Embedded into Polyimide of Intrinsic Microporosity

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Although cesium lead halide perovskite (CsPbX_3 , $X = \text{Cl, Br, or I}$) nanocrystals (PNCs) have been rapidly developed for multiple optoelectronic applications due to their outstanding optical and transport properties, their device fabrication and commercialization have been limited by their low structural stability, especially under environmental conditions. In this work, a new approach has been developed to protect the surface of these nanocrystals, which results in enhanced chemical stability and optical properties. This method is based on the encapsulation of CsPbX_3 NCs into a polyimide with intrinsic microporosity (PIM-PI), 4,4'-(hexafluoroisopropylidene)diphthalic anhydride reacted with 2,4,6-trimethyl-*m*-phenylenediamine (6FDA-TrMPD). The presence of 6FDA-TrMPD as a protective layer can efficiently isolate NCs from an air environment and subsequently enhance their optical and photoluminescence stability. More specifically, comparing NCs treated with a polymer to as-synthesized nanocrystals after 168 h, we observe that the PL intensity decreased by 70% and 20% for the NCs before and after polymer treatment. In addition, the PNC film with a polymer shows a much longer excited-state lifetime than the as-synthesized nanocrystals, indicating that the surface trap states are significantly reduced in the treated PNCs. The enhancement in chemical and air stability, as well as optical behavior, will further improve the performance of CsPbBr_3 PNCs yielding promising optical devices and paving the way for their production and implementation at a large scale.

1. Introduction

In recent years, researchers have focused on the development of various lead-based perovskite materials for optoelectronic applications [1–5] due to their remarkable optical properties, including high photoluminescence quantum yields (PLQYs), narrow emission bands (*i.e.*, small full width at half – maximum (FWHM) < 30 nm), and tunable bandgaps over the entire UV-visible-near IR spectral region [6–12]. Among the perovskite materials of increasing interest, inorganic lead-based perovskite nanocrystals (PNCs) have drawn the attention of researchers because they have bandgaps that can be tuned by exchanging halide ions and

changing the PNC size, their great optical performance, and easy synthesis methods. They have become promising semiconducting materials for light-emitting diodes (LEDs) [13–19], photodetectors [20–24], scintillators [25–29], and lasers [30–36]. However, their commercialization in devices is still restricted by the poor stability of PNC-based films [37–39]. PNCs are quite sensitive to organic polar solvents and water due to their inherent ionic nature, and they partially or entirely lose their surface ligands or structural integrity in polar solvents [40–42]. In this case, PNC films are also not stable against light irradiation, oxygen, and heat exposure [42–44]. Moreover, the organic ligands could detach from the PNC surface during spin-coating, giving

SCHEME 1: Synthesis of the 6FDA-TrMPD polymer by the polycondensation of 6FDA and TrMPD in *m*-cresol.

rise to surface defects that make the films less stable [45]. To address these issues, different strategies have been developed to overcome the stability issue, including doping, surface engineering, and matrix encapsulation (*e.g.*, polymer encapsulation or inorganic encapsulation) [45–50].

Among the aforementioned strategies, polymer encapsulation has recently gained great attention, as perovskite-polymer composites exhibit high environmental stability. In addition, the surface defects of PNCs could be passivated by polymers, achieving a significant enhancement in PL intensity [46, 51]. Due to the compatibility between polymers and perovskites, various composites have been fabricated and studied [49–51]. For instance, Snaith *et al.* mixed as-synthesized inorganic PNCs with polystyrene (PS) and polymethyl methacrylate (PMMA) [47] in order to prevent anion exchange and increase air stability. Kovalenko *et al.* studied multiple polymer effects through single CsPbBr₃ PNC light emission on optical stability. This study suggested that the proper choice of polymers in perovskite film preparation could help improve device performance [52]. After that, Yang *et al.* applied the thick polymer poly(maleic anhydride-*alt*-1-octadecene) on CsPbBr₃ PNCs as a protection layer. The PL intensity of the film remains at 90% from the original after 144 h, and the film has been applied as white LEDs with high performance [53]. In addition, Lin and coworkers applied a copolymer nanoreactor strategy for crafting perovskite nanocrystals composited with the polymer poly(acrylic acid)-*block*-polystyrene, which is able to protect nanocrystals from air and water [54]. Note that polymers that have been used to enhance NC stability are nonporous polymers or porous polymers synthesized together with NCs. There are no reports about posttreatment polymers with intrinsic microporosity (PIMs) to boost NC stability and performance.

Herein, we propose and test a postsynthesis strategy to embed CsPbBr₃ PNCs into porous polymers to enhance the surface stability and maintain the optical properties of PNC films. Steady-state and time-resolved spectroscopy results confirm the improvement in NC stability after treatment. The selected polymer, an intrinsically microporous polyimide (6FDA-TrMPD), was synthesized *via* the polycondensation reaction of 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and 2,4,6-trimethyl-*m*-phenylenediamine (TrMPD). This polyimide is able to accommodate perovskite NCs and act as a shell surround, leading to much fewer surface defects and improved air stability. This approach can improve the chemical stability of perovskite and other sensitive materials and make their everyday applications more feasible.

2. Materials and Methods

2.1. Material and Nanocrystal Synthesis. All the following reagents were used without any purification: Cs₂CO₃ (cesium carbonate, 99%, Sigma-Aldrich), OA (oleic acid, 90%, Sigma-Aldrich), OAm (oleylamine, 90%, Sigma-Aldrich), PbBr₂ (lead bromide, 99.99%), ODE (1-octadecene, 90%, Sigma-Aldrich), TOL (toluene, 99.8%, Sigma-Aldrich), DCM (dichloromethane, 99.5%, Sigma-Aldrich), PMMA (polymethyl methacrylate, Sigma-Aldrich), 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA, 99%, Merck), 2,4,6-trimethyl-*m*-phenylenediamine (TrMPD, 96%, Merck), *m*-cresol (99%, Merck), isoquinoline (97%, Merck), methanol (MeOH, analytical standard, Merck), and chloroform (CH₃Cl, analytical standard, Merck).

CsPbBr₃ PNCs were synthesized by the hot-injection method. First, 0.203 g of Cs₂CO₃ was loaded into a 50 ml round bottom flask with 10 ml of ODE and 0.625 ml of OA. The solution was stirred and degassed at 120°C under vacuum for 1 h until all Cs₂CO₃ was dissolved to obtain a clear solution as a cesium oleate precursor. PbBr₂ (350 mg) was loaded into a flask with 25 ml of ODE, and the mixture was dried under vacuum for 1 hour at 120°C. OA (2.5 ml) and OAm (2.5 ml) were injected with purging N₂, and the solution was stirred until PbBr₂ was fully dissolved. The temperature was raised to 180°C, and 2 ml of the cesium oleate precursor was quickly injected. After 5 seconds of reaction, the flask was cooled in an ice-water bath. After the ice-water bath, the solution was centrifuged at 10000 rpm for 5 min, washed with TOL, and centrifuged again. The PNCs were collected by dispersion in 3 ml of TOL.

2.2. Porous Polymer Synthesis. Intrinsically microporous polyimide 6FDA-TrMPD was prepared via a polycondensation reaction at high temperature, as previously reported [55]. 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and 2,4,6-trimethyl-*m*-phenylenediamine (TrMPD, 96%) were mixed in equimolar amounts (0.665 mmol each) in *m*-cresol and heated to 80°C under continuous nitrogen flow. A catalytic amount of isoquinoline was added, and the reaction was conducted at 200°C for a few hours. The highly viscous polymer solution was cooled down and poured into MeOH. The polymer powder was further purified by reprecipitation from its CHCl₃ solution to MeOH. The final off-white powder (0.36 g, yield = 90%) was dried at 150°C under vacuum for 24 hours. The polymer exhibited good solubility in chloroform, dichloromethane, tetrahydrofuran, dimethylformamide, dimethylacetamide, and N-methyl-2-pyrrolidone. ¹H NMR (400 MHz, DMSO-

FIGURE 1: (a, b) TEM images of as-synthesized PNCs and CsPbBr₃ perovskite NCs with the polymer. (c, d) Size distribution histogram of as-synthesized PNCs and CsPbBr₃ perovskite NCs with the polymer. (e, f) Experimental XRD pattern (black) of as-synthesized PNCs and CsPbBr₃ perovskite NCs with the polymer. The red XRD patterns are the calculated patterns.

d_6): δ 1.93 (s, 3H), 2.15 (s, 6H), 7.33 (s, 1H), 7.94 (s, 4H), 8.19 (s, 2H). FT-IR (ν , cm^{-1}): 2844–2922 (C–H str), 1794 (C=O asym, str), 1728 (C=O sym, str), 1359 (C–N, str); $M_n = 104,000 \text{ g mol}^{-1}$; $M_w = 187,000 \text{ g mol}^{-1}$; PDI = 1.79; $S_{\text{BET}} = 480 \pm 20 \text{ m}^2 \text{ g}^{-1}$; TGA analysis: $T_{d,5\%} = 503^\circ\text{C}$.

2.3. Film Preparation. The 6FDA-TrMPD solution was prepared by dissolving 12 mg of 6FDA-TrMPD polyimide in 1 ml of DCM, and 12 mg of PMMA was dissolved in 1 ml of DCM. The PNCs with a polymer solution were prepared by mixing 1 ml of CsPbBr_3 PNCs in a TOL solution and 250 μl of a 6FDA-TrMPD solution. The NCs with a PMMA solution were prepared by mixing 1 ml of CsPbBr_3 NCs in a TOL solution and 250 μl of a PMMA solution. The pure PNC solution was prepared with 1 ml of a CsPbBr_3 solution and 250 μl of DCM. The solution was spin-coated on a glass substrate in a nitrogen environment at 3000 rpm for 30 seconds.

2.4. Time-Resolved Photoluminescence Lifetime. To understand the polymer coating effect on the PNC luminescent properties, we performed PL lifetime measurements on films using the time-correlated single-photon counting technique. The samples were excited at 405 nm with a ps-pulsed. The PL signal was monitored at 510 nm using a bandpass filter. The interpulse duration was 10 MHz, and the intensity of the pulses was adjusted to detect less than 1% of excitation events. The time resolution of the system is 120 ps. A detailed description of the system can be found in the Supporting Information.

2.5. Femtosecond Transient Absorption. The phenomena taking place early upon PNC excitation were obtained through femtosecond transient absorption (fs-TA) spectroscopy. For this purpose, the samples were excited with 480 nm pulses generated with an optical parametric amplifier pumped by an amplified Ti:sapphire laser (800 nm, 100 fs, 1 kHz). The pump fluence ($0.5 \mu\text{J cm}^{-2}$) was adjusted to prevent the generation of multiple charge carriers. The probe pulses (white light) were generated by passing another fraction of the 800 nm beam through a 2 mm-thick CaF_2 crystal. The white light was split into two beams (signal and reference). The excitation pump pulses spatially overlapped with the probe pulses on the samples after passing through a synchronized mechanical chopper (500 Hz), which blocked alternative pump pulses. The obtained signal was sent to the detector through an optical fiber. A detailed description of the system can be found in the Supporting Information.

3. Results and Discussion

Porous polyimide (6FDA-TrMPD) was synthesized by a one-pot high-temperature polycondensation reaction (see Scheme 1) and used as an incubator to enhance nanocrystal stability without inducing any structural changes. The total conversion of poly(amic) acid to polyimides was achieved at 200°C . The conversion was confirmed by the absence of ^1H NMR peaks above 10 ppm (Figure S1) [55].

The polyimide structure was also confirmed using ^1H NMR and FTIR (see Figure S1 and Figure S2). It is worth

FIGURE 2: (a) PL intensity decay of the as-synthesized CsPbBr_3 PNC film. (b) PL intensity decay of the CsPbBr_3 PNC film with the polymer. (c) Time-resolved PL (excitation wavelength = 400 nm) of NC films with and without the polymer treatment.

pointing out that 6FDA-TrMPD displays high porosity, a Brunauer-Emmett-Teller surface area of $480 \text{ m}^2 \text{ g}^{-1}$, and high thermal stability, with a 5% degradation temperature of 503°C (see Figure S3 and Figure S4). 6FDA-TrMPD has

FIGURE 3: Fs-TA spectra (a), (b) 2D color plot, (c) spectra with a subhundred ps time delay, and (d) normalized bleach recovery kinetics at 512 nm of CsPbBr₃ PNC films with and without the polymer in response to 480 nm laser excitation.

a pore size distribution ranging from 0.5 nm to 120 nm, with significant porosity ranges in the mesoporous area for pore sizes between 40 nm and 120 nm, which is suitable for accommodating PNCs. The large BET surface area, high

thermal stability, and suitable pore size make 6FDA-TrMPD a promising material for embedding and protecting NCs.

To understand the interaction between PNCs and 6FDA-TrMPD during the mixing process, after preparing PNCs

SCHEME 2: Scheme of as-synthesized CsPbBr₃ NCs and NCs with 6FDA-TrMPD postsynthesis treatment.

with and without polymer, they were also characterized and tested to confirm their structural and optical properties. To investigate the structural change of PNCs after polymer treatment, high-resolution transmission electron microscopy (HR-TEM) was performed. As shown in Figures 1(a) and 1(b), the HR-TEM images reveal that PNCs have a cubic shape, which is consistent with previous reports [6, 7, 12]. Also, the size distribution of PNCs was 10.5 ± 1.5 nm after polymer treatment, which was comparable to that of PNCs without treatment, with a size distribution of 10.9 ± 1.2 nm (see Figures 1(c) and 1(d)). This result suggests that the polymer does not interact or modify the morphology or size of the CsPbBr₃ PNCs, making it a suitable coating material for PNCs. It should be noted that the length of the ligand (oleic acid and oleylamine) is ~ 2 nm, and the average size of the PNCs is ~ 11 nm. Considering that the average pore size of the polymer is more than 40 nm, it will be able to capture at least one or two PNCs per pore.

X-ray diffraction (XRD) patterns were also used to determine the PNC structure before and after polymer treatment (Figures 1(e) and 1(f)). The XRD patterns of the films of as-synthesized PNCs and PNCs mixed with the polymer were compared with standard CsPbBr₃ XRD patterns. In comparison, they exhibited exactly the same peaks. It should be noted that nanocrystal samples have different orientations and different environments, which could lead to a change in the relative intensity of XRD peaks. This indicates that the porous polymer did not change or modify the structure or the dimensionality of the CsPbBr₃ NCs. These results again confirm that the polymer only provides a coating for the PNCs. Therefore, the polymer treatment does not affect the NC structure or size.

We further investigated the stability of CsPbBr₃ PNC films by performing steady-state and time-resolved spectroscopic measurements. The steady-state PL spectra and time-resolved PL decay of as-synthesized and polymer-treated PNCs were collected within 168 h at 40% humidity and 23°C following 375 nm excitation. The as-synthesized PNC films without and with polymer exhibit 63.58% and 61.34% PLQY, respectively. It would mean that there is no immediate effect on the PLQY by the polymer encapsulation. As shown in Figure 2, the film with as-synthesized PNCs

lost 70% of its initial PL intensity. On the other hand, the film with PNCs and the porous polymer lost only 20% of its initial PL intensity (Figures 2(a) and 2(b)). It is important to mention that both samples display their peak maxima at 510 nm, confirming that the polymeric coating does not alter the main PNC structure. Interestingly, the film with PNCs treated with PMMA was also tested to compare it with porous polymer to study the importance of porous structure, in which the nanocrystal lost 40% of its original PL intensity (Figure S6). This observation highlights the importance of the pore size of 6FDA-TrMPD, which can provide better protection for PNCs and enhance PNC stability.

Furthermore, the PL lifetimes of the CsPbBr₃ PNC film with and without the polymer after 168 h are drastically different, as observed in Figure 2(c). After 168 h, the PL lifetime at 510 nm of the PNCs with the porous polymer is much longer than that of the PNCs without the polymer. More specifically, for the film without the polymer, the lifetime dropped from 5.80 ± 0.12 ns to 3.67 ± 0.07 ns, and for the film with the polymer, the lifetime decay exhibited no significant variation, changing from 5.60 ± 0.10 ns to 5.86 ± 0.13 ns (see Figure 2(c)). This observation indicates that the porous polymer successfully preserved the optical properties of the CsPbBr₃ PNCs in an air environment after 168 h. The last results confirm that our method can serve as a promising way to protect PNCs in films and effectively enhance their chemical resistance while maintaining their desired luminescent behavior.

After confirming the notable effect of polymer encapsulation on the enhancement in the luminescent stability of the CsPbBr₃ PNC film, a further examination was performed through fs-TA in order to understand the changes in PNC excited-state dynamics and the effect of the polymer on the charge carrier recombination of the PNC film. Femtosecond time-resolved laser spectroscopy has been widely used to convey detailed information on the relaxation of the excited state in photoactive materials. Therefore, the effect of the 6FDA-TrMPD polymer on the perovskite optical properties was studied by the transient absorption technique. Figures 3(a) and 3(b) portray the 2D color plot of the fs-TA measurements of CsPbBr₃ films

with and without the polymer obtained in response to 480 nm optical excitation. A persistent ground state bleaching signal appears at 512 nm, which can be attributed to the effect of band filling, which agrees well with the optical bandgap (2.3 eV) and the result obtained from steady-state optical absorption spectra (see Figure S7).

As shown in Figures 3(a)–3(c), the ground-state recovery time is much longer for CsPbBr₃ PNC films treated with the polymer than for untreated ones, which is consistent with PL experiments and further supports the significant role of the polymer in protecting the surface PNCs and subsequently reducing the surface trapping centers. The bleach recovery kinetics of the CsPbBr₃ film with the polymer can be fitted by a biexponential function with time constants of 212 and 1670 ps, whereas the NCs without the polymer need an additional component to be fitted appropriately; the time constants obtained were 45.7, 264, and 1860 ps. The new sub-100 ps time constant (45.7 ps) for the CsPbBr₃ film without the polymer takes half of the amplitude of the total signal with picosecond timescale, which can be assigned to a trapping process not observed for the polymer-treated film. The absence of short-lifetime components in PNC films with 6FDA-TrMPD makes the lifetime longer, and the origin of these short components might be caused by surface defects formed after ligand detachment. Different surface passivation enhancing the lifetime and having long lifetime components have been applied to PNCs by previous researchers [56, 57]. Similarly, 6FDA-TrMPD was able to accommodate the PNCs, preserve the surface, and prevent surface defects from forming during 168 h of storage. This significant difference again shows the dramatic effect of the polymer in PNCs on the early excited-state dynamics and suggests the essential role of the polymer in protecting the PNC surface. Thus, we can conclude that the 6FDA-TrMPD polymer enhanced the optical stability of the PNC film under environmental conditions, and polymer treatment could prevent ligand detachment, which is responsible for decreasing the overall photoluminescence quantum yield.

Scheme 2 illustrates the mechanism of the enhancement in the optical stability for the PNC film; mesoporous 6FDA-TrMPD with a suitable pore size (more than 40 nm) can accommodate the CsPbBr₃ PNCs to enhance their stability, similar to other polymers. Similar to PMMA, 6FDA-TrMPD can protect the PNCs from air environments. After protection, PNCs were embedded into porous polymer, which maintains the surface of PNCs and reduces ligand detachment during film preparation, which causes less degradation of PL intensity. In addition, polymers with pore size greater than 40 nm can capture one or two PNCs in a single pore. This feature can significantly prevent NC aggregation and can preserve the surface of PNCs. The ligands of CsPbBr₃ nanocrystals have nonpolar end chains, and all nonpolar and carbonyl groups of the polyimide are not activated to interact with other sites. Polymer pore size as 40 nm is larger than PNCs with around 15 nm, meaning they do not form a compact core-shell structure. The porous polymer may not fully isolate all of PNCs, so the film might be conductive for further application as optical devices. Based on these two factors, 6FDA-TrMPD shows better stability

enhancement than PMMA and maintains the optical properties in the film phase.

In summary, a polyimide with intrinsic microporosity, 6FDA-TrMPD, has been developed as a new treatment approach to significantly enhance the optical properties and photostability of CsPbBr₃ perovskite nanocrystal films. The charge carrier dynamics and the optical stability of PNC films were studied through time-resolved PL and fs-transient absorption measurements. The results demonstrated that the porous polymer coating could prevent ligand detachment and subsequently preserve the surface stability. Moreover, we find that the polymer also plays a fundamental role in inhibiting surface trapping deactivation processes. This method enables porous polymers to significantly enhance the optical stability and chemical resistance of perovskite nanocrystals for their use as potential optoelectronic devices, including LEDs, scintillators, and lasing devices. The approach proposed here is a step contributing to overcoming the persistent challenge of stability in inorganic perovskite materials and can be used as a starting point to increase the commercial use of these highly efficient luminescent materials.

Data Availability

The authors declare that the main data supporting the findings in this study are available within the article and its supplementary information. Additional data are available from the corresponding authors upon reasonable request.

Conflicts of Interest

The authors declare no competing financial interest.

Authors' Contributions

O.F.M., O.M.B., G.S., and Y.H. proposed the project, designed the experiment, and revised the manuscript. H.Y. synthesized PNCs, prepared films, carried out characterizations, and wrote the manuscript. L.G.A., P.M., and Y.Z. performed optical measurements including time-resolved photoluminescence, transient absorption spectroscopy, and photoluminescence characterization. M.A.A. prepared and characterized the porous polymer. J.Y. prepared the figures, helped in discussing the results, and revised the manuscript. C.C. carried out the TEM characterizations.

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Supplementary Materials

Figure S1: ¹H NMR spectrum of the intrinsically microporous polyimide 6FDA-TrMPD in deuterated dimethylsulfoxide (DMSO-d₆). Figure S2: FT-IR spectrum of 6FDA-TrMPD. Figure S3: thermal decomposition profile of 6FDA-TrMPD polyimide in a nitrogen atmosphere. Figure S4: nitrogen adsorption isotherm of 6FDA-TrMPD obtained from ASAP

2020 at -198°C and up to 1 bar. The BET surface area was calculated using the relative pressure range between 0 and 0.3. Figure S5: pore size distribution of 6FDA-TrMPD obtained from ASAP 2020 using NLDFT. Figure S6: the PL intensity of CsPbBr_3 perovskite nanocrystals with PMMA treatment decreased after 168 h. Figure S7: PL decay during 168 h and steady-state absorption with and without the polymer. (Supplementary Materials)

References

- [1] A. Kojima, K. Teshima, Y. Shirai, and T. Miyasaka, "Organometal halide perovskites as visible-light sensitizers for photovoltaic cells," *Journal of the American Chemical Society*, vol. 131, no. 17, pp. 6050–6051, 2009.
- [2] J. Burschka, N. Pellet, S. J. Moon et al., "Sequential deposition as a route to high-performance perovskite-sensitized solar cells," *Nature*, vol. 499, no. 7458, pp. 316–319, 2013.
- [3] M. Liu, M. B. Johnston, and H. J. Snaith, "Efficient planar heterojunction perovskite solar cells by vapour deposition," *Nature*, vol. 501, no. 7467, pp. 395–398, 2013.
- [4] J. S. Manser, J. A. Christians, and P. V. Kamat, "Intriguing optoelectronic properties of metal halide perovskites," *Chemical Reviews*, vol. 116, no. 21, pp. 12956–13008, 2016.
- [5] W. Ke and M. G. Kanatzidis, "Prospects for low-toxicity lead-free perovskite solar cells," *Nature Communications*, vol. 10, 2019.
- [6] Q. A. Akkerman, V. D'Innocenzo, S. Accornero et al., "Tuning the optical properties of cesium lead halide perovskite nanocrystals by anion exchange reactions," *Journal of the American Chemical Society*, vol. 137, no. 32, pp. 10276–10281, 2015.
- [7] L. Protesescu, S. Yakunin, M. I. Bodnarchuk et al., "Nanocrystals of cesium lead halide perovskites (CsPbX_3 , $\text{X} = \text{Cl, Br, and I}$): novel optoelectronic materials showing bright emission with wide color gamut," *Nano Letters*, vol. 15, no. 6, pp. 3692–3696, 2015.
- [8] J. Shamsi, A. S. Urban, M. Imran, L. De Trizio, and L. Manna, "Metal halide perovskite nanocrystals: synthesis, post-synthesis modifications, and their optical properties," *Chemical Reviews*, vol. 119, no. 5, pp. 3296–3348, 2019.
- [9] L. Protesescu, S. Yakunin, O. Nazarenko, D. N. Dirin, and M. V. Kovalenko, "Low-cost synthesis of highly luminescent colloidal lead halide perovskite nanocrystals by wet ball milling," *ACS Applied Nano Materials*, vol. 1, no. 3, pp. 1300–1308, 2018.
- [10] L. N. Quan, R. Quintero-Bermudez, O. Voznyy et al., "Highly emissive green perovskite nanocrystals in a solid state crystalline matrix," *Advanced Materials*, vol. 29, no. 21, article 1605945, 2017.
- [11] F. Di Stasio, S. Christodoulou, N. Huo, and G. Konstantatos, "Near-unity photoluminescence quantum yield in CsPbBr_3 nanocrystal solid-state films via postsynthesis treatment with lead bromide," *Chemistry of Materials*, vol. 29, no. 18, pp. 7663–7667, 2017.
- [12] H. Yang, Y. Zhang, J. Pan, J. Yin, O. M. Bakr, and O. F. Mohammed, "Room-temperature engineering of all-inorganic perovskite nanocrystals with different dimensionalities," *Chemistry of Materials*, vol. 29, no. 21, pp. 8978–8982, 2017.
- [13] X. Zheng, S. Yuan, J. Liu et al., "Chlorine vacancy passivation in mixed halide perovskite quantum dots by organic pseudohalides enables efficient red-emitting diodes," *ACS Energy Letters*, vol. 5, no. 3, pp. 793–798, 2020.
- [14] T. Chiba, Y. Hayashi, H. Ebe et al., "Anion-exchange red perovskite quantum dots with ammonium iodine salts for highly efficient light-emitting devices," *Nature Photonics*, vol. 12, no. 11, pp. 681–687, 2018.
- [15] Y. Cao, N. Wang, H. Tian et al., "Perovskite light-emitting diodes based on spontaneously formed submicrometre-scale structures," *Nature*, vol. 562, no. 7726, pp. 249–253, 2018.
- [16] J. Li, L. Xu, T. Wang et al., "50-Fold EQE improvement up to 6.27% of solution-processed all-inorganic perovskite CsPbBr_3 QLEDs via surface ligand density control," *Advanced Materials*, vol. 29, no. 5, article 1603885, 2017.
- [17] E. Yassitepe, Z. Yang, O. Voznyy et al., "Amine-free synthesis of cesium lead halide perovskite quantum dots for efficient light-emitting diodes," *Advanced Functional Materials*, vol. 26, no. 47, pp. 8757–8763, 2016.
- [18] G. Li, F. W. Rivarola, N. J. Davis et al., "Highly efficient perovskite nanocrystal light-emitting diodes enabled by a universal crosslinking method," *Advanced Materials*, vol. 28, no. 18, pp. 3528–3534, 2016.
- [19] J. Song, J. Li, X. Li, L. Xu, Y. Dong, and H. Zeng, "Quantum dot light-emitting diodes based on inorganic perovskite cesium lead halides (CsPbX_3)," *Advanced Materials*, vol. 27, no. 44, pp. 7162–7167, 2015.
- [20] L. Lv, Y. Xu, H. Fang et al., "Generalized colloidal synthesis of high-quality, two-dimensional cesium lead halide perovskite nanosheets and their applications in photodetectors," *Nanoscale*, vol. 8, no. 28, pp. 13589–13596, 2016.
- [21] X. Li, D. Yu, J. Chen et al., "Constructing fast carrier tracks into flexible perovskite photodetectors to greatly improve responsivity," *ACS Nano*, vol. 11, no. 2, pp. 2015–2023, 2017.
- [22] M. Shoaib, X. Zhang, X. Wang et al., "Directional growth of ultralong CsPbBr_3 perovskite nanowires for high-performance photodetectors," *Journal of the American Chemical Society*, vol. 139, no. 44, pp. 15592–15595, 2017.
- [23] A. Waleed, M. M. Tavakoli, L. Gu et al., "All inorganic cesium lead iodide perovskite nanowires with stabilized cubic phase at room temperature and nanowire array-based photodetectors," *Nano Letters*, vol. 17, no. 8, pp. 4951–4957, 2017.
- [24] C. Bao, J. Yang, S. Bai et al., "High performance and stable all-inorganic metal halide perovskite-based photodetectors for optical communication applications," *Advanced Materials*, vol. 30, no. 38, article 1803422, 2018.
- [25] Q. Chen, J. Wu, X. Ou et al., "All-inorganic perovskite nanocrystal scintillators," *Nature*, vol. 561, no. 7721, pp. 88–93, 2018.
- [26] J. H. Heo, D. H. Shin, J. K. Park, D. H. Kim, S. J. Lee, and S. H. Im, "High-performance next-generation perovskite nanocrystal scintillator for nondestructive X-ray imaging," *Advanced Materials*, vol. 30, no. 40, article 1801743, 2018.
- [27] J. Liu, B. Shabbir, C. Wang et al., "Flexible, printable soft-X-ray detectors based on all-inorganic perovskite quantum dots," *Advanced Materials*, vol. 31, no. 30, article 1901644, 2019.
- [28] Y. Zhang, R. Sun, X. Ou et al., "Metal halide perovskite nanosheet for X-ray high-resolution scintillation imaging screens," *ACS Nano*, vol. 13, no. 2, pp. 2520–2525, 2019.
- [29] D. Yu, P. Wang, F. Cao et al., "Two-dimensional halide perovskite as β -ray scintillator for nuclear radiation monitoring," *Nature Communications*, vol. 11, 2020.

- [30] S. Li, D. Lei, W. Ren et al., "Water-resistant perovskite nanodots enable robust two-photon lasing in aqueous environment," *Nature Communications*, vol. 11, no. 1, pp. 1192–1198, 2020.
- [31] L. Jiang, R. Liu, R. Su et al., "Continuous wave pumped single-mode nanolasers in inorganic perovskites with robust stability and high quantum yield," *Nanoscale*, vol. 10, no. 28, pp. 13565–13571, 2018.
- [32] X. Tang, Z. Hu, W. Yuan et al., "Perovskite CsPb₂Br₅ Microplate laser with enhanced stability and tunable properties," *Advanced Optical Materials*, vol. 5, no. 3, article 1600788, 2017.
- [33] W. Zheng, P. Huang, Z. Gong et al., "Near-infrared-triggered photon upconversion tuning in all-inorganic cesium lead halide perovskite quantum dots," *Nature Communications*, vol. 9, no. 1, pp. 3462–3469, 2018.
- [34] S. A. Veldhuis, P. P. Boix, N. Yantara et al., "Perovskite materials for light-emitting diodes and lasers," *Advanced Materials*, vol. 28, no. 32, pp. 6804–6834, 2016.
- [35] H. Zhu, Y. Fu, F. Meng et al., "Lead halide perovskite nanowire lasers with low lasing thresholds and high quality factors," *Nature Materials*, vol. 14, no. 6, pp. 636–642, 2015.
- [36] J. Pan, S. P. Sarmah, B. Murali et al., "Air-stable surface-passivated perovskite quantum dots for ultra-robust, single- and two-photon-induced amplified spontaneous emission," *The Journal of Physical Chemistry Letters*, vol. 6, no. 24, pp. 5027–5033, 2015.
- [37] F. Lang, O. Shargaieva, V. V. Brus, H. C. Neitzert, J. Rappich, and N. H. Nickel, "Influence of radiation on the properties and the stability of hybrid perovskites," *Advanced Materials*, vol. 30, no. 3, article 1702905, 2018.
- [38] H. Cho, Y. H. Kim, C. Wolf, H. D. Lee, and T. W. Lee, "Improving the stability of metal halide perovskite materials and light-emitting diodes," *Advanced Materials*, vol. 30, no. 42, article 1704587, 2018.
- [39] N. H. Tiep, Z. Ku, and H. J. Fan, "Recent advances in improving the stability of perovskite solar cells," *Advanced Energy Materials*, vol. 6, no. 3, article 1501420, 2016.
- [40] J. De Roo, M. Ibanez, P. Geiregat et al., "Highly dynamic ligand binding and light absorption coefficient of cesium lead bromide perovskite nanocrystals," *ACS Nano*, vol. 10, no. 2, pp. 2071–2081, 2016.
- [41] Y. Kim, E. Yassitepe, O. Voznyy et al., "Efficient luminescence from perovskite quantum dot solids," *ACS Applied Materials & Interfaces*, vol. 7, no. 45, pp. 25007–25013, 2015.
- [42] X. Li, F. Cao, D. Yu et al., "All inorganic halide perovskites nanosystem: synthesis, structural features, optical properties and optoelectronic applications," *Small*, vol. 13, no. 9, article 1603996, 2017.
- [43] G. P. Nagabhushana, R. Shivaramaiah, and A. Navrotsky, "Direct calorimetric verification of thermodynamic instability of lead halide hybrid perovskites," *Proceedings of the National Academy of Sciences*, vol. 113, no. 28, pp. 7717–7721, 2016.
- [44] S. Zou, Y. Liu, J. Li et al., "Stabilizing cesium lead halide perovskite lattice through Mn (II) substitution for air-stable light-emitting diodes," *Journal of the American Chemical Society*, vol. 139, no. 33, pp. 11443–11450, 2017.
- [45] Y. Wei, Z. Cheng, and J. Lin, "An overview on enhancing the stability of lead halide perovskite quantum dots and their applications in phosphor-converted LEDs," *Chemical Society Reviews*, vol. 48, no. 1, pp. 310–350, 2019.
- [46] Y. H. Song, J. S. Yoo, B. K. Kang et al., "Long-term stable stacked CsPbBr₃ quantum dot films for highly efficient white light generation in LEDs," *Nanoscale*, vol. 8, no. 47, pp. 19523–19526, 2016.
- [47] S. Pathak, N. Sakai, F. Wisnivesky Rocca Rivarola et al., "Perovskite crystals for tunable white light emission," *Chemistry of Materials*, vol. 27, no. 23, pp. 8066–8075, 2015.
- [48] M. Kulbak, S. Gupta, N. Kedem et al., "Cesium enhances long-term stability of lead bromide perovskite-based solar cells," *The Journal of Physical Chemistry Letters*, vol. 7, no. 1, pp. 167–172, 2016.
- [49] H. Liao, S. Guo, S. Cao et al., "A general strategy for in situ growth of all-inorganic CsPbX₃ (X= Br, I, and Cl) perovskite nanocrystals in polymer fibers toward significantly enhanced water/thermal stabilities," *Advanced Optical Materials*, vol. 6, no. 15, article 1800346, 2018.
- [50] C. C. Lin, D. H. Jiang, C. C. Kuo et al., "Water-resistant efficient stretchable perovskite-embedded fiber membranes for light-emitting diodes," *ACS Applied Materials & Interfaces*, vol. 10, no. 3, pp. 2210–2215, 2018.
- [51] Y. Li, Y. Lv, Z. Guo et al., "One-step preparation of long-term stable and flexible CsPbBr₃ perovskite quantum dots/ethylene vinyl acetate copolymer composite films for white light-emitting diodes," *ACS Applied Materials & Interfaces*, vol. 10, no. 18, pp. 15888–15894, 2018.
- [52] G. Raino, A. Landuyt, F. Krieg et al., "Underestimated effect of a polymer matrix on the light emission of single CsPbBr₃ nanocrystals," *Nano Letters*, vol. 19, no. 6, pp. 3648–3653, 2019.
- [53] H. Wu, S. Wang, F. Cao et al., "Ultrastable inorganic perovskite nanocrystals coated with a thick long-chain polymer for efficient white light-emitting diodes," *Chemistry of Materials*, vol. 31, no. 6, pp. 1936–1940, 2019.
- [54] Y. J. Yoon, Y. Chang, S. Zhang et al., "Enabling tailorable optical properties and markedly enhanced stability of perovskite quantum dots by permanently ligating with polymer hairs," *Advanced Materials*, vol. 31, no. 32, article 1901602, 2019.
- [55] M. A. Abdulhamid, G. Genduso, Y. Wang, X. Ma, and I. Pinnau, "Plasticization-resistant carboxyl-functionalized 6FDA-polyimide of intrinsic microporosity (PIM-PI) for membrane-based gas separation," *Industrial & Engineering Chemistry Research*, vol. 59, no. 12, pp. 5247–5256, 2020.
- [56] D. N. Dirin, L. Protesescu, D. Trummer et al., "Harnessing defect-tolerance at the nanoscale: highly luminescent lead halide perovskite nanocrystals in mesoporous silica matrixes," *Nano Letters*, vol. 16, no. 9, pp. 5866–5874, 2016.
- [57] S. Wang, Y. Wang, Y. Zhang et al., "Cesium lead chloride/bromide perovskite quantum dots with strong blue emission realized via a nitrate-induced selective surface defect elimination process," *The Journal of Physical Chemistry Letters*, vol. 10, no. 1, pp. 90–96, 2019.