Research Article

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

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Although cesium lead halide perovskite (CsPbX3, X = 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 CsPbX3 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 CsPbBr3 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
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 composed 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)diphalic anhydride (6FDA) and 2,4,6-trimethyl-m-phenylenediamine (TrMPD). This polyimide is able to accommodate perovskite NCs and act as a shell surrounding, 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)diphalic 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 h 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 s 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)diphalic 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 h. 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 CsPbBr$_3$ perovskite NCs with the polymer. (c, d) Size distribution histogram of as-synthesized PNCs and CsPbBr$_3$ perovskite NCs with the polymer. (e, f) Experimental XRD pattern (black) of as-synthesized PNCs and CsPbBr$_3$ perovskite NCs with the polymer. The red XRD patterns are the calculated patterns.
δ (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); $M_n = 104,000$ g mol⁻¹; $M_w = 187,000$ g mol⁻¹; PDI = 1.79; $S_{BET} = 480 ± 20$ m² g⁻¹; TGA analysis: $T_{d,5%} = 503$ °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 CsPbBr₃ 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 CsPbBr₃ NCS in a TOL solution and 250 μl of a PMMA solution. The pure PNC solution was prepared with 1 ml of a CsPbBr₃ 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 μJ 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 CaF₂ 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 pointing out that 6FDA-TrMPD displays high porosity, a Brunauer-Emmett-Teller surface area of 480 m² g⁻¹, and high thermal stability, with a 5% degradation temperature of 503°C (see Figure S3 and Figure S4). 6FDA-TrMPD has
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...

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 CsPbBr$_3$ PNC films with and without the polymer in response to 480 nm laser excitation.
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 CsPbBr$_3$ 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 CsPbBr$_3$ 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 CsPbBr$_3$ 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 CsPbBr$_3$ 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 CsPbBr$_3$ 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 CsPbBr$_3$ 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 CsPbBr$_3$ 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 CsPbBr$_3$ films.
CsPbBr₃ nanocrystals have nonpolar end chains, and all non-
and can preserve the surface of PNCs. The ligands of
pore. This feature can signi

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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
reducing the surface trapping centers. The bleach recovery
time is much longer for CsPbBr₃
polymer than for untreated ones, which is consistent with PL
experiments 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
copolymer 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 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 trap-
ning 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 con-
clude 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 photolumines-
cence 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 stabil-
ity, 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 degra-
dation 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 non-
polar 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 con-
ductive for further application as optical devices. Based on
these two factors, 6FDA-TrMPD shows better stability
enhancement than PMMA and maintains the optical proper-
ties 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 inhibit-
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 pro-
posed 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 find-
ings in this study are available within the article and its sup-
plementary 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 characteriza-
tions, and wrote the manuscript. L.G.A., P.M., and Y.Z. per-
formed optical measurements including time-resolved
photoluminescence 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: 1HNMR 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)

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