Air-Stable Surface-Passivated Perovskite Quantum Dots
for Ultra-Robust, Single- and Two-Photon-Induced
Amplified Spontaneous Emission

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ABSTRACT: We demonstrate ultra-air- and photostable CsPbBr$_3$ QDs by using an inorganic-organic hybrid ion pair as the capping ligand. This passivation approach to perovskite QDs yields high photoluminescence quantum yield with unprecedented operational stability in ambient conditions (60 ± 5% lab humidity) and high pump fluences, thus overcoming one of the greatest challenges impeding the development of perovskite-based applications. Due to the robustness of passivated perovskite QDs, we were able to induce ultra-stable amplified spontaneous emission (ASE) in solution processed QD films not only through one photon but also through two-photon absorption processes. The latter has not been observed before in the family of perovskite materials. More importantly, passivated perovskite QD films showed remarkable photostability under continuous pulsed laser excitation in ambient conditions for at least 34 hours (corresponds to $1.2 \times 10^8$ laser shots), substantially exceeding the stability of other colloidal QD systems in which ASE has been observed.

TOC GRAPHICS

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Lead trihalide perovskite materials with the formula $\text{APbX}_3$ (where $A=\text{Cs}^+, \text{CH}_3\text{NH}_3^+$, or $\text{HC(NH}_2\text{)}_2^+$; $X=\text{Br}^-, \text{I}^-$, and/or $\text{Cl}^-$) have recently emerged as promising materials for solution-processed optoelectronic applications such as photovoltaics,$^1$-$^6$ lasing,$^7$-$^{10}$ light-emitting diodes$^{11}$-$^{14}$ and photodetectors$^{15}$-$^{17}$ because of their easily tunable optical bandgap as well as their attractive absorption, emission, and charge transport properties$^{18}$. $\text{APbX}_3$ materials$^{19}$ with some, or all, of these characteristics, have been realized in various forms, including thin films,$^{20}$ single crystals,$^{21}$-$^{22}$ nanowires,$^{23}$-$^{24}$ and quantum dots.$^{25}$-$^{26}$ Perovskite QDs in particular, such as $\text{CsPbX}_3$, have ushered the advantages of perovskite materials into the realm of quantum confinement. The results are QDs with emission lines that exhibit narrow full widths at half maximum (FWHM) and remarkably high photoluminescence quantum yields (PLQYs) (approximately $\geq 70\%$) and yet can be easily tuned over a very broad spectral window.$^{27}$-$^{30}$

Despite the impressive metrics of the entire family of lead trihalide perovskites$^{31}$, however, poor stability, in particular with respect to temperature, moisture, and light exposure, remains a ubiquitous impediment for virtually all $\text{APbX}_3$ perovskite materials and devices.$^{32}$-$^{33}$ The lack of stability has not only prevented the practical and commercial application of perovskite optoelectronics but has also constrained the exploration of their properties to highly sanitized conditions.$^{34}$ Under such a restrictive regime, non-linear optical properties essential for lithography$^{35}$, high-resolution optical microscopy,$^{36}$ and the characterization and generation of ultrafast optical signals$^{37}$ suffer the most. For the aforementioned reasons, surface passivation strategies of perovskite materials have been vigorously pursued (for example, Snaith et. al employed various organic Lewis bases such as thiophene and pyridine to passivate the surface of perovskite films to achieve high photovoltaic power conversion efficiency),$^{38}$ but to date, none have led to operational and long-term stability under ambient conditions and/or at high optical fluence.

Herein, we report the development of ultra-air- and photostable perovskite QDs through a new passivation technique (Fig. 1) in which the surface of QDs is coated with an inorganic-organic hybrid ion pair.$^{39}$ This novel approach yields high photoluminescence quantum yield (PLQY) with
remarkably high operational stability in ambient conditions (60 ± 5% lab humidity) and high pump fluences, thus overcoming one of the major challenges impeding the development of perovskite-based applications. By achieving such levels of robustness, we were able to induce with no signs of degradation amplified spontaneous emission (ASE) in solution-processed QD films not only through one photon (1PA) but also through two-photon absorption (2PA) processes. ASE with the latter in particular has not been previously reported before in the family of perovskite materials, and it demonstrates the potential of these materials for non-linear optical applications.

CsPbBr$_3$ quantum dots (QDs) were synthesized similarly to the modified hot-injection method previously reported by Protesescu et al.$^{27}$ As shown in Figure 1, selective centrifugation of the crude solution yielded three samples of various QD sizes. Size distribution analysis revealed the presence of three different populations of QDs (referred to as samples 1, 2 and 3) with average sizes of ~8.2 nm, 9.2 nm, and ~10.6 nm, respectively (Figure S1). To investigate the quantum
size effect, we measured the photoluminescence spectra of the synthesized samples. Clear red spectral shifts of 9 nm and 16 nm were observed in the PL position of samples 2 and 3, relative to the spectrum of sample 1, which is consistent with quantum confinement (Figure S2). This observation is in line with recent reports on the same type of QDs.26-27

The passivation of surface defects in nanosized organometal halide perovskites can lead to a substantial increase in the photoluminescence quantum yield (PLQY) at room temperature40; however, the air and photostabilities of these materials remained elusive. The current study aimed to improve both the PLQY and stability by passivating the QDs, a prerequisite for using them in optoelectronic applications. Initially, we observed that the synthesized CsPbBr₃ QDs displayed a lower PLQY compared to previously reported values.27 Moreover, the PLQY depended on the size of the QDs, reaching values of approximately 35%, 49% and 49% for samples 1, 2 and 3, respectively. To overcome these critical issues, we introduced an inorganic-organic hybrid ion pair (di-dodecyl dimethylammonium sulfide, S²⁻-DDA⁺)41 to passivate the QDs, di-dodecyl dimethyl ammonium bromide (DDAB) was used as a source of DDA⁺ (see the experimental section in the sulfur precursor part) to passivate the perovskite CsPbBr₃ QDs. While inorganic-organic hybrid ion pairs, such as AsS₃³⁻-DDA⁺, where used to cap metal chalcogenide nanocrystal39, their implementation for perovskite materials has not been demonstrated. In this method, 50 µl of oleic acid (OA) was added to 1 mL of CsPbBr₃ QDs (15 mg/mL) under stirring, followed by the addition of a certain amount of sulfur precursor (see Experimental Section for details). The reaction product was subsequently precipitated with BuOH and re-dissolved in octane. We observed that the solution PLQY was enhanced from 49% to 70% upon the injection of 100 µl of sulfur precursor (Figure S3b). Notably the original position of the emission peak of the CsPbBr₃ QDs remained almost unaltered upon the addition
of the sulfur precursor, and only an enhancement was observed (Figure S3a). To understand the nature and the composition of the surface passivation, we employed energy-filtered TEM (EFTEM) analysis, from which we observed that sulfur plays a role in passivation (Figure S4). Also, CHNS elemental analysis further corroborated the existence of sulfur upon treatment (Table S1). Also, the molar ratio of N, C and H in treated sample is about 1: 26: 56, which is consistent with that of didodecyldimethylammonium ion (DDA\(^+\)), confirmed the formation of ion-pair ligand (S\(^2^-\)-DDA\(^+\)).

The untreated and treated samples were characterized by X-ray powder diffraction (XRD). The XRD patterns of both the samples were well indexed to the standard cubic CsPbBr\(_3\) phase, with no observable secondary phases (Figure S5). The instability and degradation of an untreated QD sample were also substantiated by X-ray fluorescence (XRF) analysis, as indicated by the 1:2:5 atomic ratios of Cs, Pb, and Br, respectively, a considerable deviation from the 1:1:3 ratio expected for perovskites (Table. S2). Moreover, treated samples were noticeably brighter than the untreated samples under UV light, a clear indicator of the high luminescence obtained after passivation (Figure S6).
Figure 2. (a) Absorption and PL spectra of CsPbBr$_3$ QD film before and after surface treatment. (b) TEM image of treated QD. (c) TEM image of untreated QD.

For optical characterizations, the untreated and treated samples were spin-coated on a glass substrate to obtain a uniform thin film (see Experimental Section). Figure 2a shows the absorption and photoluminescence (PL) spectra of the QD films before and after surface passivation. It should be noted that the PL signal is quite narrow in both cases, with an FWHM of 25 nm. Only a very slight change in the bandgap could be observed, as shown in the Tauc plot (Figure 2, inset), suggesting that the particle size was essentially preserved even after the surface treatment. In addition to the characterizations performed by electronic spectroscopy, vibrational spectroscopy was used to probe the specific chemical functionalities on the surface of the QDs. The C=O stretching vibration of OA was used as a specific marker mode to probe the ligand
exchange process. In this experiment, the absence of the $1680 \text{ cm}^{-1}$ peak (C=O stretching) in the FTIR spectrum of the treated sample (Figure S7) provided a clear indication of the replacement of the native oleate functional group by the hybrid ion pair.

To confirm the air and photostability of the passivated CsPbBr$_3$ QDs films (thickness $\sim$105 nm, Figure S8), we tested their propensity for amplified spontaneous emission (ASE) through one- and two-photon pumping under ambient conditions (room temperature, 60±5% humidity). The results are shown in Figure 3. As can be seen, with an increase in the pump fluence, the ASE generated at 533 nm shifted to 537 nm, which is consistent with the results of a previous report.$^{42}$ The onset of stimulated emission in the QD films was observed with the immediate increase in the ASE intensity (ASE peak at $\approx$533 nm) and the narrowing of the emission spectrum (FWHM $\approx$ 4–7 nm, Figure 3a inset) over the threshold pumping range. A red shift in the ASE peak (16-21 nm) relative to the PL peak was observed (Figure 3a).

As shown in Figure 4a, the ASE threshold fluence for one-photon pumping was approximately 192 $\mu$J/cm$^2$, which is lower than the value reported for perovskite thin films.$^{43}$ On the other hand, the threshold obtained for the QD film in the current study is higher than that recently reported for the same QDs,$^{42}$ probably due to differences in the configurations of the experimental setups. However, the air and photostabilities of our treated QDs are the best reported to date for semiconductor QDs and even for perovskite thin films. It is worth noting that the untreated sample suffered from partial degradation within hours, showing a sharp contrast in performance, whereas the passivated QD film exhibited the same threshold and optical characteristics even after 4 months of open air storage and rounds of photostability testing (vide infra and also see Figure S9), providing clear evidence of the ultra-stability of perovskite QD films under ambient conditions.
Figure 3. Pump-fluence relationship determined for the treated CsPbBr$_3$ QD film in (a) 1PA and (b) 2PA.
To test the photostability of our QDs films, we measured the variation in ASE intensity as a function of time under continuous femtosecond laser irradiation in ambient conditions, using a femtosecond laser system operated at a repetition rate of 1 kHz. Our results showed that there was almost no change in ASE intensity over \(1.2 \times 10^8\) laser shots (corresponding to a period of 34 hours) for either one- or two-photon pumping (Figure 5). This value substantially exceeds the photo-stability of other semiconductor QD systems for which ASE has been observed.\(^{44,45}\)

We studied the excited-state dynamics of QDs by the time-correlated single photon counting (TCSPC) technique. At pump fluences below the ASE threshold (8.5 \(\mu J/cm^2\), Supplementary Information, figure S10), typical PL lifetime of 11 ns was observed. Well above the ASE threshold (220 \(\mu J/cm^2\); Figure S10), an ASE lifetime of approximately 2.8 ns was recorded, which further decreased to 1.9 ns with the increase in pump fluence. Such a fast decay with increasing pump fluence could be attributed to the dominant contribution from the non-radiative decay channel.

We further investigated the pumping of the passivated perovskite QDs with a non-linear 2PA scheme. Note that 2PA is a third-order non-linear optical phenomenon in which a molecule absorbs two photons simultaneously, resulting in an electronic transition from the ground state to an excited state via virtual states. 2PA pumping has several advantages over 1PA pumping, for instance, minimum risk of photodamage to the sample, longer penetration depth in the absorbing material and the absence of a phase-matching requirement for the generation and wavelength tuning of coherent light.\(^{45}\) In addition to these advantages, deleterious effects of the excitation light such as unwanted scattering and absorption losses are completely suppressed in 2PA.
Figure 4. Threshold behavior of the intensity of the ASE of the treated CsPbBr$_3$ QD film in (a) 1PA and (b) 2PA.

The ASE-induced in the perovskite QDs during optical pumping was achieved via 2PA at 800 nm. The following wavelength range highlights the distinct advantages offered by 2PA pumping for the perovskite QDs because high-powered laser sources are abundant within this range; moreover, the range is also an optical transparency window for water and biological media. It is
worth noting that below and above the threshold fluence, the FWHM and peak position achieved through 2PA pumping are indistinguishable from those achieved by 1PA excitation; however, a decrease in the intensity of the ASE achieved by 2PA was observed. Femtosecond transient absorption with broadband capabilities shows that the dynamics of 2PA-induced ground-state bleaching were similar to those of 1PA, and the recovery time fits a single exponential function with a characteristic time constant of \(\sim 20 \text{ ns}\) (Figure S11).

Although the excited-state dynamics were observed to be identical, 1PA and 2PA ASE showed markedly different thresholds. For two-photon excitation, the ASE threshold fluence was 12 mJ/cm\(^2\) (Figure 4b), which is comparable to that reported for 2PA ASE in other semiconductor QDs.\(^{46}\) Nevertheless, the stability of our passivated perovskite QDs under the applied operating conditions largely surpasses (photostability unchanged after \(1.2 \times 10^8\) laser shots) all previously reported levels for ASE in QDs, regardless of whether 1PA or 2PA induced that emission. Although few reports on the 2PA pumping of colloidal QDs exist\(^{45,47-49}\) ASE from 2PA pumping in the perovskite family of materials has not been reported prior to this work.
Figure 5. Shot-dependent ASE intensity of the solution-processed CsPbBr3 QDs film with approximately $1.2 \times 10^8$ laser excitation shots at (254 µJ/cm$^2$ pump fluence for 1PA, 18 mJ/cm$^2$ pump fluence for 2PA) performed at room temperature under ambient conditions.

In summary, a passivation strategy for lead halide perovskite QDs was developed to alleviate the inherent instability of the material when operating under ambient conditions currently is the
greatest challenge impeding the development of perovskite-based devices. Our passivation strategy is endowed perovskite QDs with unprecedented stability in the air (60 ± 5% humidity) and under high laser fluences, with samples showing no noticeable degradation. An analytical investigation of the passivated perovskite QDs revealed the formation of a protective layer enriched with sulfide (S^{2-}-DDA^+). Because of the ultra-high stability of the resulting QDs, we were able to induce ultra-stable ASE in solution-processed QD films not only by 1PA but also by a 2PA process. ASE in the latter is a phenomenon that has yet to be observed in any perovskite material. Additionally, our perovskite QD films showed significant photo-stability under continuous pulsed laser excitation in ambient conditions for at least 34 hours (corresponds to 1.2 x 10^8 laser shots), substantially exceeding the stability of other colloidal QD systems in which ASE has been observed. The described QD passivation strategy and multiphoton-induced processes enable the practical implementation of perovskite QDs and facilitate the exploration of both their linear and non-linear applications. We believe that this surface passivation mechanism and the validity of the 2PA process will open new avenues of study and hold promise for overcoming the greatest problem precluding the development of perovskite-based materials for solar cell and non-linear applications.

EXPERIMENTAL SECTION

Synthesis

1-butanol (BuOH, HPLC grade), was purchased from Fisher Scientific. Oleic acid (OA, technical grade 90%), lead bromide (PbBr_2, 98%) and octane (98%) were purchased from Alpha Aesar. Sodium sulfide hydrate, cesium carbonate (Cs_2CO_3, 99.995%, metal basis), di-dodecyl dimethyl ammonium bromide (DDAB, 98%), oleylamine (OLA, technical grade 70%), and 1-octadecene (ODE, technical grade 90%) were purchased from Sigma-Aldrich. Toluene (HPLC
grade) was purchased from Honeywell Burdick & Jackson. All chemicals were used as procured without further purification.

**Preparation of Cs-oleate**

Cs$_2$CO$_3$ (0.814 g) along with ODE (40 mL) and OA (2.5 mL) were loaded into a 100 mL two-neck flask, dried for 1 h at 120 ºC, and then heated under N2 at 150 ºC until all Cs$_2$CO$_3$ had reacted with OA. The solution was maintained at 150 ºC before injection to prevent the solidification of Cs-oleate.

**Preparation of S precursor (S$^{2-}$-DDA$^+$)**

Similarly to Jiang’s method,$^{41}$ 3 mL of toluene containing 0.15 m mol of DDAB was mixed with 3 mL of 50 mM aqueous Na$_2$S solution. The S$^{2-}$ anions were then transferred from the aqueous phase to the toluene phase. The toluene phase was separated and used as a sulfur precursor (DDA-S$^{2-}$) in subsequent experiments.

**Synthesis of CsPbBr$_3$ QDs**

In contrast to the methods reported elsewhere$^{27,32}$ in the current study, the OLA and OA were not pre-dried, and not all solvents used were anhydrous. ODE (125 mL) and PbBr$_2$ (1.725 g) were loaded into a 500 mL two-neck round-bottom flask and dried under vacuum for 1 h at 120 ºC. OLA (12.5 mL) and OA (12.5 mL) were then injected at 120 ºC under N$_2$. After the PbBr$_2$ salt had completely dissolved, the temperature was raised to 180 ºC, and Cs-oleate solution (10 mL, prepared as described above) was quickly injected; an ice-water bath was then used to cool the reaction mixture after 5 seconds.

**Selected purification of CsPbBr$_3$ QDs**
The crude solution was cooled in a water bath and directly transferred to centrifuge tubes. After centrifuging the tubes at 7000 rpm for 15 min, the supernatant and precipitate were collected separately. The supernatant was mixed with BuOH for centrifugation, and the bottom sample was then collected and re-dissolved in toluene (sample 1). The precipitate was dispersed by adding toluene to collect the new supernatant (sample 2) after centrifugation and re-disperse the new precipitate in toluene (sample 3).

*Treatment of CsPbBr$_3$ QDs and Preparation of CsPbBr$_3$ QDs films*

To 1 mL of the different CsPbBr$_3$ QDs (15 mg/mL), 50 µL of OA was added under stirring. A certain amount of sulfur precursor was then added sequentially. The sample was precipitated with twice the amount of BuOH and re-dissolved in 200 µL of octane. Thin films of CsPbBr$_3$ QDs were obtained by spin-coating the treated CsPbBr$_3$ QD solution under ambient conditions onto glass substrates. Moreover, the untreated sample was washed with BuOH alone and re-dissolved in octane to fabricate the thin films. The glass substrates were cleaned by standard procedure with detergent, de-ionized water, acetone, and isopropanol. The cleaned substrates were treated with plasma for 5 min before depositing the QD films. Highly smooth, densely packed and pinhole-free thin films were obtained by spin-coating at 500 rpm (10 sec) and then at 1500 rpm (40 sec).

*Characterization*

UV-vis absorption spectra were obtained using an absorption spectrophotometer from Ocean Optics. Carbon, hydrogen, oxygen, and sulfur analysis was performed using a Flash 2000 elemental analyzer (Thermo Fischer Scientific). Photoluminescence was tested using an FLS920 dedicated fluorescence spectrometer from Edinburgh Instruments. Quantum yield was measured using an Edinburgh Instruments integrating sphere with an FLS920-s fluorescence spectrometer.
FTIR was performed using a Nicolet 6700 FT-IR spectrometer. Powder X-ray diffraction (XRD) patterns were recorded using Siemens diffractometer with Cu Kα radiation (λ=1.54178 Å). TEM analysis was carried out with a Titan™ TEM (FEI Company) operating at a beam energy of 300 keV and equipped with a Tridiem™ post-column energy filter (Gatan, IQD.). The samples were imaged in energy-filtered TEM (EFTEM) mode with a 20 eV energy slit inserted around the zero-energy-loss electrons to acquire high-resolution TEM (HRTEM) micrographs. The spatial distribution of the elements Pb and S was determined and acquired using the EFTEM technique by selecting the Pb O-edge (86 eV) and S L-edge (165 eV) in the three-window mapping method. Morphological investigations and cross-sectional imaging of the QD films were carried out on a Karl Zeiss FESEM.

**Experimental details of optical pumping, single photon counting and transient absorption**

All ASE pumping experiments were conducted at room temperature. The 1PA pumping experiments were performed using a femtosecond laser system operated at a wavelength 800 nm with 35 fs pulses and a repetition rate of 1 kHz. UV pump pulses at 400 nm were obtained in a straightforward manner by the second harmonic (frequency doubled) of the fundamental beam, where 100 µJ of the laser output was focused in a 100 µm BBO nonlinear crystal. The 2PA pumping experiments were carried out by directly using the fundamental beam at 800 nm.

Time-correlated single photon counting (TCSPC) for lifetime measurements was performed using a Halcyone MC multichannel fluorescence up-conversion spectrometer (Ultrafast Systems) at an excitation wavelength of 400 nm. Nanosecond transient absorption experiments were conducted using an EOS setup (Ultrafast Systems). Detailed information regarding the experimental setup has been published elsewhere.50-51
ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website. The data underpinning the results presented in this manuscript can be accessed free of charge at http://pubs.acs.org

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REFERENCES


