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Tunable fluorescence and optical nonlinearities of all inorganic colloidal cesium lead

halide perovskite nanocrystals

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Abstract

The formation of cesium lead halide perovskite nanocrystals are very effortless due to its extremely fast reaction kinetics. Herein, we present simple hot-inject approach and anion exchange reaction to fabricate all inorganic colloidal CsPbX₃ perovskite nanocrystals (NCs). The colloidal CsPbX₃ NCs with controlling-size exhibit the characteristics of the high luminescent intensity, superior quantum yields (QY, above 69%) and the narrow-band emission tuning, the bandgap energies and emission spectra are readily tunable over the entire visible spectral region of 425-710 nm. Moreover, the third-order nonlinear optical properties of all inorganic colloidal perovskite nanocrystals (CsPbCl₃, CsPbBr₃, CsPbI₃) were measured using the Z-scan technique, indicating excellent third-order optical nonlinearities. Nonlinear optical susceptibilities reaching to 3.78 × 10⁻¹¹ esu for CsPbBr₃ NCs, figure of merit is achieving above 5 for CsPbI₃ NCs. These interesting results demonstrate that the as-prepared all inorganic colloidal CsPbX₃ perovskite nanocrystals are expected to hold great promise for application on nonlinear optoelectronic devices.

Keywords: Cesium lead halide, nanocrystal, tunable fluorescence, optical nonlinearity, Z-scan technique

1. Introduction

The metal halide perovskite NCs have presented superior performance in the fields of fluorescent light [1,2,3], polarized emission [4], photodetector [5,6], LED [7-10] and laser [11-14]. This arouses the interest in the comprehension of the optical characters of these materials. Previous works have demonstrated that the photoluminescence (PL) in CsPbX₃ (X being either Cl, Br, I or a combination of both) NCs, which show that the band gap energies and emission spectra of perovskite NCs are readily tunable over the whole visible spectra region [2,14]. The PL of CsPbX₃ NCs are characterized by strong light absorption, narrow emission line widths, high QY, and short radiative lifetimes [15, 16, 17]. Kovalenko and the co-workers firstly reported

a new synthetic process to fabricate all inorganic colloidal CsPbX₃ NCs last year, they obtained the samples by reacting Cs-oleate with Pb-halide in a high boiling solvent at 140-200 $^{\circ}$ C [2]. After that, on account of the fast kinetics of CsPbX₃ perovskite nanoparticle growth, different composite methods of CsPbX₃ NCs have been used, such as anion exchange reactions and supersaturated recrystallization at room temperature [18, 19, 20]. Owing to the relative moderation and accuracy, the hot-injection approach and anion exchange reaction are effective methods to prepare CsPbX₃ NCs.

Recently, people found that the lead halide perovskites show great performance in nonlinear optics [21, 22]. The researches of nonlinear optical materials are mainly concentrating on amorphous glasses [23], organic substances and some uncommon materials [24], such as inert gases [25], alkali metal atomic vapor and liquid crystal [26,27]. In contrast with the traditional nonlinear materials, halide anions in metal lead tri-halide perovskite NCs can be easily extracted and exchanged with another ones [5]. Basanth and the co-workers systematically studied on the nonlinear optical properties of organic-inorganic (OI) lead halide perovskites [28], which indicated the OI perovskites have large nonlinear refractive index and saturable absorption properties. This study identified the OI lead halide perovskites have promising applications in the field of nonlinear optics in addition to the numerous investigation about solar cells and the optical modulator. Wang and the co-workers compared the nonlinear optical properties of colloidal CH₃NH₃PbBr₃ and CsPbBr₃ quantum dots, and they indicated that OI lead bromine presents relative high nonlinear optical susceptibilities than CsPbBr₃ because of photoinduced orientation effects [29]. Whereas, although both OI and all-inorganic materials possess a resemblant direct optical band gap, CsPbBr₃ demonstrates a higher thermal stability than MAPbBr₃ for OI lead halide perovskite NCs should be kept dispersible in a wide range of organic solvents [30,31], enhancing device lifetime in application. In general, these two families of colloidal perovskites, OI lead halide NCs and all-inorganic CsPbX₃ NCs, feature their respective advantages and properties. Unfortunately, the devices of CsPbX₃ are mainly focus on CsPbBr₃ rather than CsPbCl₃ or CsPbI₃, stimulating our desire to systematically study the nonlinear characteristic in different halogen of CsPbX₃.

In this paper, we present a simple approach to fabricate all-inorganic colloidal CsPbX₃ NCs through the

hot-injection combining anion exchange reaction, and systematically investigate the component dependence of the halogen on the PL properties in all-inorganic colloidal CsPbX₃ NCs. Moreover, the third-order nonlinear optical characteristics of CsPbX₃ NCs (CsPbCl₃, CsPbBr₃, CsPbI₃) were measured via using the Z-scan technique, and the results exhibited that CsPbBr₃ NCs possess strong third-order nonlinearity susceptibility and high value of figure of merit. Accordingly, CsPbX₃ NCs materials are shown to be appropriate for all-optical switches and optical limiting devices.

2. Experimental section

2.1 Synthesis of CsPbX₃.

2.1.1 Preparation of Cs-oleate. The preparation process is similar to the previous report by Protesescu with slight revision here [2]. Cs_2CO_3 (0.814 g, Aladdin, 99%), oleic acid (OA 2.5 mL, Aladdin, 85%) and octadecene (ODE 40 mL, Aladdin, 90%) were added into a 100 mL 3-neck flask, dried for 1 h at 120 °C and then stored under N₂. Since Cs-oleate precipitates out of ODE at room-temperature, it must be preheated to 100 °C before injection into reaction flask.

2.1.2 Synthesis of CsPbX₃ NCs. Dried ODE (5 mL) and different amounts of PbX₂ (0.069 g, PbBr₂, ABCR, 98%; PbI₂, 0.087 g, ABCR, 99.999%) were loaded into a 25 mL 3-neck flask and degassed at 120 °C for 1 h. Dried OA (0.5 mL) and oleylamine (OAm 0.5 mL, Aladdin, 85%) were injected at 120 °C under N₂ flow. After complete solubilization of the PbBr₂ or PbI₂ salt, the temperature was raised to 160 °C and Cs-oleate solution (0.4 mL of stock solution prepared as described above) was swiftly injected and then (about 5 seconds) the reaction mixture was cooled down by the water bath. Importantly, it has been reported that CsPbCl₃ can be fabricated by CsPbBr₃ using anion exchange reaction, neither did CsPbI₃ [5, 20]. Chlorine anion exchange reaction was carried out at room temperature using lithium chloride to exchange bromine.



Fig. 1. The synthesis schematic of CsPbX₃ NCs (X = Cl, Br, I).

2.1.3 Isolation and purification of CsPbX₃ NCs. The crude solution cooled down with water bath and the aggregated NCs were separated by centrifuging, and the addition of tert-butanol (t-BuOH, Aladdin, 99%) to the crude solution (ODE:t-BuOH = 1:1 by volume) were found to be helpful for a complete precipitation. After centrifugation, the supernatant was discarded and the precipitates were re-dispersed in hexane to form long-term stable colloidal solutions for the following measurements.

2.2 Instrumentation.

To explore the crystalline structure of the colloidal perovskites had formed, X-ray diffraction (XRD) analysis was performed on a Germany Bruker X-ray diffractometer (operation voltage and current were 40 kV and 40 mA) with Cu K_a radiation ($\lambda = 1.5418$ Å). The radiation at a scan was at the rate of 0.02° s⁻¹ in the range of 10–60°. Transmission electron microscopy (TEM) images were carried out on a FEI Tecnai G2 F20 S-TWIN transmission electron microscope operating at an acceleration voltage of 200 kV. The linear optical absorption of the NCs in the wavelength range of 200-800 nm was obtained at room temperature by a PerkinElmer Lambda 750 UV-vis Spectrometer. Fluorescence spectra and PL QY were recorded with a Horiba Jobin Yvon Fluromax-4P spectrophotometer equipped with absolute QY measurement apparatus. Time-resolved PL lifetime measurements were carried out using a time-correlated single-photon counting (TCSPC) lifetime spectroscopy system with a nanosecond-pulsed diode laser (nanoLED-370) as the single wavelength excitation light source. X-ray photoelectron spectroscopy (XPS) measurement was obtained using AXI ULTRA DLD spectrometer with monochrome Al Ka as the excitation source. For nonlinear study, we used a femtosecond Q-switched laser (Spectra Physics Explorer), operating at a wavelength of 787 nm in TEM00 operation mode. The repetition frequency was fixed at 1 kHz, pulse width of 396 fs and the Z-scan with the operating power levels have been typically greater than 3 mW.

3. Results and discussion

CsPbBr₃ and CsPbI₃ NCs are formed by direct hot-injection synthesis at 160 °C, while CsPbCl₃ are compounded through exchanging bromine anion with chlorine anion in our work. Perovskite CsPbX₃ NCs are recognized to crystallize in orthorhombic, tetragonal, and cubic crystal, and colloidal CsPbX₃ NCs crystallize in cubic crystal [2, 32] (**Fig. 2a**). **Fig. 2b** reveals the XRD patterns of CsPbX₃ NCs, which keep the similar profile in the range of 10-60° ($2\theta = 14.6^{\circ}$ and 30.1° correspond to diffractions formed at (100) and (200) planes for CsPbBr₃, $2\theta = 15.4^{\circ}$ and 30.9° for CsPbCl₃, $2\theta = 14.1^{\circ}$ and 28.6° for CsPbI₃) owing to their same crystal structure. The XRD pattern of CsPbI₃ brings out the PbI₂ diffraction peaks ($2\theta =$ 12.8° and 26.7° correspond to diffractions formed at (001) and (011) planes) in **Fig. 2b**, but no extra phase is found in CsPbBr₃ and CsPbCl₃ NCs, attributing to that the lead triiodide perovskite has a higher reaction enthalpy [33]. This shows CsPbBr₃ and CsPbCl₃ NCs possess more stable structure than CsPbI₃ NCs, and they are to be preferred as a practical device into application. Notably, it is also found that the diffraction peak at (100) and (200) planes slightly shift to the smaller 2 θ angle from CsPbCl₃ to CsPbI₃, which is attributed to the lattice expansion by the substitution of larger ion for the smaller ion (r₁ > r_{Br} > r_{C1}), indicating that halides ions redistributed congeneric throughout the NCs [11], according to Braggs equation.

$\mathbf{n}\boldsymbol{\lambda} = 2\mathbf{d}\mathbf{s}\mathbf{i}\mathbf{n}\boldsymbol{\theta} \tag{1}$

Remarkably, some refraction peaks in the XRD patterns disappear in comparison with the corresponding standard phase (CsPbBr₃, PDF#54-0752,), which is ascribed to the preferential orientation assembly of perovskite CsPbX₃ causing to the appearance of some stronger peaks with the (100), (110) and (200) lattice plans [34].



Fig. 2. Colloidal CsPbX₃ NCs dispersed in hexane and their structural characterization. (a) Schematic of the cubic perovskite lattice of CsPbBr₃. (b) XRD patterns for typical ternary and mixed-halide CsPbX₃ NCs.

Fig. 3 shows the TEM and HR-TEM images of colloidal CsPbX₃ NCs as well as the size distribution. **Fig. 3a**, **3c**, and **3e** clearly show that the CsPbCl₃ NCs are obtained via anion exchange reaction retain the parental construction CsPbBr₃ and CsPbI₃ NCs. As TEM images depict, the growth durations yield cubic phase of CsPbX₃ NCs, and the average side length are 28.7 nm, 21.4 nm, and 15.2 nm of CsPbI₃, CsPbBr₃, and CsPbCl₃ NCs, respectively. The insets in **Fig. 3a**, **3c**, and **3e** highlight the selected area electron diffraction (SAED), providing the diffractive images which correspond to the cubic crystal form of CsPbX₃. To characterize the NCs microstructure from the crude reaction, the distinct lattice fringes are observed in the HR-TEM images of **Fig. 3b**, **3d**, and **3f**, including (101) spaced by 4.0 Å, (002) spaced by 2.8 Å for CsPbCl₃, (110) spaced by 4.3 Å, (200) spaced by 2.9 Å for CsPbBr₃, (120) spaced by 3.6 Å and (111) spaced by 4.4 Å for CsPbI₃. XRD pattern and TEM images indicate that we have prepared the CsPbX₃ NCs (X = Cl, Br, and I) successfully.



Fig. 3. TEM images of the parent. (a) CsPbI₃ NCs and (c) CsPbBr₃ NCs and halide exchange synthesized (e) CsPbCl₃ NCs. Inset: Selected area electron diffraction pattern obtained from part a, c, e, respectively. HR-TEM images of (b) CsPbI₃ NCs, (d) CsPbBr₃, and (f) CsPbCl₃ NCs.

In addition, XPS was carried out to further confirm the valence states of cesium, lead, and halogen of colloidal CsPbX₃ NCs in hexane. **Fig. 4** represents the survey scan XPS spectra of cesium, lead and halogen, respectively. No significant differences are observed among those obtained spectra for the Cs 3d and Pb 4f. **Fig. 4a** shows the Cs 3d peak of CsPbX₃ at 738.8 eV and 724.9 eV, corresponding to the Cs $3d_{5/2}$ and Cs $3d_{3/2}$ electron energy levels, respectively. The Pb 4f XPS peaks

(shown in **Fig. 4b**) appear as the doublet because of spin-orbit splitting for each chemical species present [35]. Interestingly, the Pb 4f spectrum obtains for the as-received sample showed two main peaks at 137.4 eV and 142.2 eV (Pb 4f_{7/2} and Pb 4f_{5/2}), while the Pb 4f spectrum of CsPbCl₃ presents two peaks (about 138.5 eV and 143.3 eV) locating at the nearby of the main peaks. **Fig. 4c**, **4d**, and **4e** show the I 3d peaks of CsPbI₃ at 619.9 eV and 631.4 eV, Br 3d peaks of CsPbBr₃ at 67.1 eV and 67.5 eV, and Cl 2p peaks of CsPbCl₃ at 197.4 eV and 198.9 eV, which correspond to the I $3d_{5/2}$ and I $3d_{3/2}$ electron energy levels, the Br $3d_{5/2}$ and Br $3d_{3/2}$ electron energy levels, Cl $2p_{3/2}$ and Cl $2p_{1/2}$ electron energy levels, respectively. In general, XPS results indicate that cesium, lead, and halogen maintain their valence states in CsPbX₃ NCs. To sum up, on the analysis of the structure and composition of colloidal NCs with the utility of XRD, TEM, and XPS, the main phases of the samples with cubic crystal and valence state were confirmed to be CsPbX₃, and these results contribute to further optical properties of the CsPbX₃ NCs.



Fig. 4. High-resolution cesium, lead, halogen XPS spectra: (a), (b) Cs 3d and Pb 4f high-resolution spectrum of CsPbCl₃, CsPbBr₃ and CsPbI₃; (c) Cl 2p, (d) Br 3d, and (e) I 3d high-resolution spectrum of CsPbCl₃, CsPbBr₃ and CsPbI₃.

In order to demonstrate the excellent luminescent properties of $CsPbX_3$ NCs, optical images of the $CsPbX_3$ NCs samples under ambient light and a 365 nm UV lamp are showed in **Fig.5a**, **5b**, and PL spectra are presented in **Fig. 5c**. For the highly luminescent colloidal NCs, $CsPbX_3$ perovskite NCs present superior QY (above 69%) and narrow emission line widths of 13-30 nm with superior size tuning of the emission peaks. The PL emission spectra of the hybrid $CsPbX_3$ (X = Cl, Br, I or a

combination of both) NCs present emission peaks at the range of 425-710 nm, hence $CsPbX_3$ NCs can produce saturated colors by controlling the composition of halogen [2]. Moreover, the overall PL intensity and optical density of the NCs do not rise anymore after 5 seconds, indicating that changing time cannot control the size in conventional batch syntheses [16]. In addition, absorption spectra of $CsPbX_3$ (X = Cl, Br, I) are showed in **Fig. 6**, consistent with the PL spectra.



Fig. 5. The samples of Color-tunable $CsPbX_3$ NCs and wide PL spectra. (a),(b) Optical images of $CsPbX_3$ NCs under ambient light and a 365 nm UV lamp. (c) PL spectra of $CsPbX_3$ NCs spanning the whole visible region with narrow emission linewidths.



Fig. 6. Uv-vis absorption spectra of CsPbCl₃, CsPbBr₃, CsPbI₃.

The PL decay curves were measured by analyzing the PL dynamics from $CsPbX_3$ NCs solution of hexane. Fig. 7 shows the time-resolved PL spectrum of $CsPbBr_{3-x}Cl_x$ and $CsPbBr_{3-x}I_x$ NCs at the peak of emission wavelength, respectively. The decays are double-exponential components with time constants (T_i) and respective amplitudes (K_i) [15]. The double-exponential decay function is calculated using equation (2), fitting accurately to the sum of double-exponential.

$\frac{\text{ACCEPTED MANUSCRIPT}}{\tau = \frac{\sum_{i} (K_{i} T_{i}^{2})}{\sum_{i} (K_{i} T_{i})}}$ (2)

The CsPbBr₃ NCs decay curve exhibits a decay time $\tau = 68.4$ ns. For the CsPbBr_{3-x}I_x series, the decay time monotonically increases to a $\tau = 252$ ns with the increasing of emission wavelength. Besides, for the CsPbBr_{3-x}Cl_x series, the decay time decrease to $\tau = 4.67$ ns with decreasing of emission wavelength when the PL emission peak at 496 nm, and the decay time increases to $\tau = 111.9$ ns when the PL emission peak at 456 nm. The results show that the decay time is sensitive to the sample fabrication process. This phenomenon may be related to localized defects in the crystals [37], thus decay time may markedly vary from sample to sample for the control of their imperfect fabrication of NCs [15].



Fig. 7. PL decay curves of the perovskite $CsPbI_{3-x}Br_x$ series NCs and $CsPbI_{3-x}Br_x$ series NCs as a typical sample in hexane measured using 370 nm excitation.

The energy band diagram of CsPbX₃ was illustrated by Kondo et al [14]. Since they elucidated the one-electron energy states of CsPbX₃ based on the molecular orbital (MO) theory applied to the octahedral Pb²⁺(X⁻)₆ quasi-complex of O_h symmetry, the prototype of the research on perovskite materials has gained great achievement. Aimed to evaluate the optical energy gap, the optical absorption coefficient $\alpha(hv)$ was obtained using the Davis and Mott equation, as shown in equation (3) [36].

$$\alpha(h v) = \frac{B(h v - E_{opt})^m}{h v}$$
(3)

B is a constant, *hv* presents the photon energy, and E_{opt} is referred as the optical band gap. *m* is a constant, which represents the type of the optical transition. **Fig. 8a** illustrates the result as a function of the photon energy by measuring the curve of the absorption coefficient. Furthermore, the straight lines are fitting curve to estimate the energy gap E_g . The discreet values of E_g are 1.73 eV, 2.39 eV, and 2.78 eV for CsPbI₃, CsPbBr₃, and CsPbCl₃, respectively. The VBMs and CBMs of CsPbX₃ (X = Cl, Br, I) are estimated, and their energy levels with respect to vacuum are depicted in **Fig. 8b**. Moving from Cl to Br to I, the VBM shifted prominently toward higher energies, while a smaller shift is observed for the CBM toward lower energies [37]. Obviously, the band alignment diagram that the change in the band gap E_g of the CsPbX₃ compounds is mainly owing to the conduction band move to higher energy, while the valence band energy remaining practically unchanged [38]. The energy gaps demonstrate that the absorption of these perovskites are in the range of visible light.



Fig. 8. (a) The spectrum plotted as $(\alpha hv)^2$ -(hv), the straight line is fitting curve to estimate the energy gap Eg. (b) A schematic energy-level diagram for CsPbX₃ (X = Cl, Br, I).

Fig. 9 represents the transmitted laser beam schematic divided by means of a beam splitter, providing the two different experimental configurations. The results of Z-scan measurements shown in Fig. 10 are carried out to determine the nonlinear refraction and absorption of the CsPbX₃ perovskites NCs samples, corresponding to open aperture (OA) curves and closed aperture (CA) curves. Ultraviolet-visible absorption spectra can be turned over the entire visible spectral region through adjusting their composition, which are shown in Fig. 6. The Z-scan technique is a single excitation beam to survey the nonlinear refractive index (NLR) and nonlinear absorption coefficient (NLA) of the materials [39]. The technique provides sensitive and straightforward measurement of the sign and the values of the nonlinear refractive index (n_0), the two-photon absorption (TPA) coefficient (β), and the free carrier absorption coefficient (σ) [40].



Fig. 9. Experimental Z-scan setup: L1, L2, and L3, lenses; BS, beam splitter; S, sample; D1 and D2, photodetectors; A, aperture.

To quantitatively measure the NLA and NLR of the CsPbX₃ (X = Cl, Br, I) NCs, **Fig. 10** exhibits the Z-scan response of the solution of CsPbCl₃, CsPbBr₃, CsPbI₃ NCs, corresponding the black dots displayed the experimental results and the red, green, and blue solid lines fitted curves in the figure fit the theoretical values of the normalized transmittance. **Fig. 10a**, **10c**, and **10e** demonstrate the OA of CsPbCl₃, CsPbBr₃, CsPbBr₃, CsPbI₃ NCs, and they all show symmetric relative to the focus (Z = 0) where it had minimum transmittance, illustrating reverse saturable absorption would emerge in the three perovskite NCs.

Fig. 10b, **10d**, and **10f** display the CA of CsPbX₃ NCs. The CA Z-scan curves with prefocal (Z < 0) minimum and the postfocal (Z > 0) maximum indicated a self-focusing process and a positive sign of NLR index ($\gamma > 0$). To depict the intensity of NLA and NLR, both β and γ of the perovskites NCs were calculated from the OA and CA Z-scan curves derived from the

ACCEPTED MANUSCRIPT Z-scan theory [41]. The real and imaginary parts of the third-order nonlinear susceptibility $\chi^{(3)}$ are deduced according to the

parameters β and γ , as shown in equations (4) and (5) [42], and the results are shown in Table 1.

$$lm x^{(3)}(esu) = \frac{\lambda \epsilon_0 c^2 n_0^2}{4\pi} \beta(m/W)$$
(4)
Re x⁽³⁾(esu) = $\frac{\epsilon_0 c^2 n_0^2}{\pi} \gamma(m/W)$ (5)

 λ , ε_0 , c, and n_0 are the wavelength of the laser light, permittivity of free space, speed of light, and linear refractive index of the perovskite NCs, respectively. For CsPbCl₃ and CsPbI₃, the value of Re $\chi^{(3)}$ is higher than Im $\chi^{(3)}$, which imply nonlinear refraction is the main third-order optical nonlinearity response in these two kinds of NCs, and they have potential application in optical switches. But for CsPbBr₃, the value of $Im \chi^{(3)}$ is higher than $Re \chi^{(3)}$, which implies nonlinear absorption is the main nonlinear behavior of CsPbBr₃ NCs, and it has potential application in optical limiting devices.



Fig. 10. Nonlinear absorption of CsPbCl₃, CsPbBr₃ and CsPbI₃ samples under irradiation of a 787 nm pulsed laser. OA (a)

CsPbCl₃, (c) CsPbBr₃, (e) CsPbI₃ NCs, and CA (b) CsPbCl₃, (d) CsPbBr₃, (f) CsPbI₃ NCs. (Theoretical data in black squares

and fitting curves in solid line).

The total optical third-order nonlinear susceptibility $\chi^{(3)}$ is given by equation (6) [41], all the values of $\chi^{(3)}$ are listed in Table 1. Obviously, the perovskites of colloidal CsPbCl₃, CsPbBr₃, CsPbI₃ NCs possess similar third-order nonlinear properties. The third-order nonlinear absorption of the three kinds of NCs exhibit reverse saturable absorption and the values of $\chi^{(3)}$ reach 2.85 × 10⁻¹¹, 3.78 × 10⁻¹¹, and 3.55 × 10⁻¹¹ esu in CsPbCl₃, CsPbBr₃, and CsPbI₃ NCs, respectively. In addition, for most of third-order nonlinear-based optical devices, nonlinear refraction is an essential parameter [43]. In our case, owing to the ultrafast pulse of 396 fs (shorter than 500 fs), accumulative thermal effects would be limited, indicating that the optical response is distinctly sensitive to the electronic ground state.

$$|x^{(3)}|(esu) = \left\{ \left[\operatorname{Re} x^{(3)} \right]^2 + \left[lm x^{(3)} \right]^2 \right\}^{1/2}$$
 (6)

Moreover, figure of merit (F) is defined to evaluate the third-order nonlinear performance of materials at a certain wavelength [44]. For the different composition of CsPbX₃, shown in table 1, the values of F reach 4.95, 1.85, 5.59, demonstrating that CsPbX₃ NCs have favorable nonlinear optical properties (the values of F are over 2 for CsPbCl₃ and CsPbI₃). Importantly, CsPbCl₃ presents a more stable structure than CsPbI₃, signifying CsPbCl₃ may possess a broader prospect for application.

Table 1. Third-order nonlinear optical parameters of the Three CsPbX₃ at 767 nm with operating power levels of 3 mW.

| sample | Wavelength (nm) | β (m/W) | γ (m²/W) | Im χ (esu) | Re χ (esu) | $\chi^{(3)}(esu)$ | F |
|---------------------|--------------------|-------------------------|-------------------------|------------------------|------------------------|-------------------------|------|
| CsPbCl ₃ | 787 1 | .36 ×10 ⁻¹³ | 5.30 ×10 ⁻¹⁹ | 1.29×10 ⁻¹¹ | 2.54×10 ⁻¹¹ | 2.85 ×10 ⁻¹¹ | 4.95 |
| CsPbBr ₃ | 787 3 | 3.22 ×10 ⁻¹³ | 4.69 ×10 ⁻¹⁹ | 3.04×10 ⁻¹¹ | 2.25×10 ⁻¹¹ | 3.78 ×10 ⁻¹¹ | 1.85 |
| CsPbI ₃ | 787 1 | .54 ×10 ⁻¹³ | 6.75 ×10 ⁻¹⁹ | 1.45×10 ⁻¹¹ | 3.24×10 ⁻¹¹ | 3.55 ×10 ⁻¹¹ | 5.59 |

In conclusion, we have investigated the fluorescent characteristic and the nonlinear optical response of the all-inorganic

perovskites CsPbX₃. Colloidal CsPbX₃ nanocrystals present highly luminescent (X = Cl, Br, I, and mixed Cl/Br and Br/I systems) with bright (QY is above 69%), stable, spectrally narrow, and broadly tunable photoluminescence (425-710 nm with a narrowing of FWHM to 13 nm-30 nm). On the basis of XRD and TEM analysis, CsPbX₃ nanocrystals exhibit the regular shift of the peak in XRD and lattice distance differences in TEM, which attributed to the same crystal structure of CsPbCl₃, CsPbBr₃, CsPbI₃ and their anion-exchange compounds. In addition, the nonlinear optical properties of the colloidal CsPbX₃NCs were determined using Z-scan and the results indicated that the NCs had excellent third-order optical nonlinearities. The $\chi^{(3)}$ of the CsPbCl₃, CsPbBr₃, CsPbI₃ were measured to be 2.85×10^{-11} , 3.78×10^{-11} , and 3.55×10^{-11} esu, and figure of merit reaching 4.95, 1.85, 5.59, respectively. Therefore, hybrid all-inorganic semiconductor perovskites CsPbX₃ have favorable nonlinear optical properties for potential use in applications such as optical switching. Future studies with these novel NCs will concentrate on increasing stability by changing tolerance factor (t) in order to apply CsPbX₃ to optoelectronic applications such as light-emitting diodes, lasers, all optical switches and photodetectors.

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Highlights

- CsPbX₃ NCs were fabricated via hot-injection combining anion exchange reaction.
- \bullet The PL properties depended on halogen in CsPbX3 NCs on have been investigated.
- CsPbX₃ NCs possess high value of figure of merit.
- CsPbX₃ NCs is a candidate of nonlinear optoelectronic devices.