

Nonlinear Absorption and Low-Threshold Multiphoton Pumped Stimulated Emission from All-Inorganic Perovskite Nanocrystals

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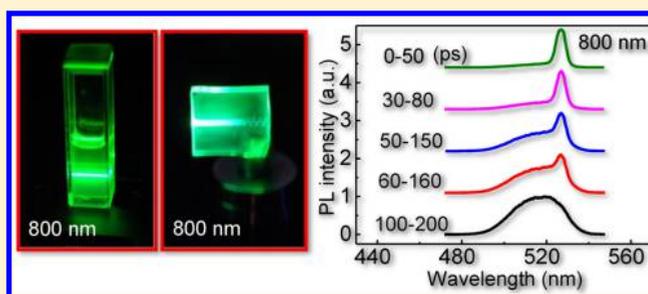
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Supporting Information

ABSTRACT: Halide perovskite materials have attracted intense research interest due to the striking performance in photoharvesting photovoltaics as well as photoemitting applications. Very recently, the emerging CsPbX₃ (X = Cl, Br, I) perovskite nanocrystals have been demonstrated to be efficient emitters with photoluminescence quantum yield as high as ~90%, room temperature single photon sources, and favorable lasing materials. Herein, the nonlinear optical properties, in particular, the multiphoton absorption and resultant photoluminescence of the CsPbBr₃ nanocrystals, were investigated. Notably, a large two-photon absorption cross-section of up to $\sim 1.2 \times 10^5$ GM is determined for 9 nm sized CsPbBr₃ nanocrystals. Moreover, low-threshold frequency-upconverted stimulated emission by two-photon absorption was observed from the thin film of close-packed CsPbBr₃ nanocrystals. The stimulated emission is found to be photostable and wavelength-tunable. We further realize the three-photon pumped stimulated emission in green spectra range from colloidal nanocrystals for the first time. Our results reveal the strong nonlinear absorption in the emerging CsPbX₃ perovskite nanocrystals and suggest these nanocrystals as attractive multiphoton pumped optical gain media, which would offer new opportunities in nonlinear photonics and revive the nonlinear optical devices.

KEYWORDS: Perovskites, nanocrystals, nonlinear absorption, stimulated emission



Halide perovskites have attracted researchers' intensive attention due to the strikingly high light-harvesting efficiency in photovoltaic in the last several years.^{1,2} Surprisingly, this new kind of semiconductors is also found to be excellent light-emitting materials, which manifests superb performance in electrically driven light-emitting diodes (LEDs) and optically pumped lasers.³⁻⁵ Until now, most of the optical studies on the halide perovskites are focusing on the linear part; however, the corresponding nonlinear optical properties are scarcely revealed.^{3,4,6-8} In contrast to linear absorption and emission, the multiphoton analogues feature several merits including a large penetration depth, high spatial resolution, and little damage to the targeted samples.⁹⁻¹¹

Recently, Sargent et al. have demonstrated the feasibility of two-photon absorption in CH₃NH₃PbBr₃ perovskite bulk crystal and suggested the perovskite crystals as potential nonlinear absorbers and emitters.¹² Quantum confined nanocrystals have long been recognized as advantageous luminescent materials thanks to the stable excitons at room temperature, large absorption cross sections, and strong oscillator

strength,¹³⁻¹⁵ contributing to the high photoluminescence quantum yield (PL QY) and low-threshold and temperature-insensitive optical gain.¹⁶⁻¹⁹ Moreover, exceptional nonlinear optical properties including strong two- and three-photon absorption are discovered from metal chalcogenide nanocrystals,^{11,20,21} which promises high-resolution bioimaging and effective frequency/wavelength conversion.^{21,22}

Very recently, the highly luminescent (PL QY of up to 90%) all-inorganic colloidal nanocrystals of cesium lead halide perovskites (CsPbX₃, X = Cl, Br, I) are emerging as a new optoelectronic material in perovskite family.²³ Compared to the traditional metal-chalcogenide nanocrystals, these emerging perovskite nanocrystals exhibit even broader (400–700 nm) PL wavelength tunability via either composition and size manipulation inherited from both halide perovskite and quantum dot; moreover, the PL wavelength tuning can be

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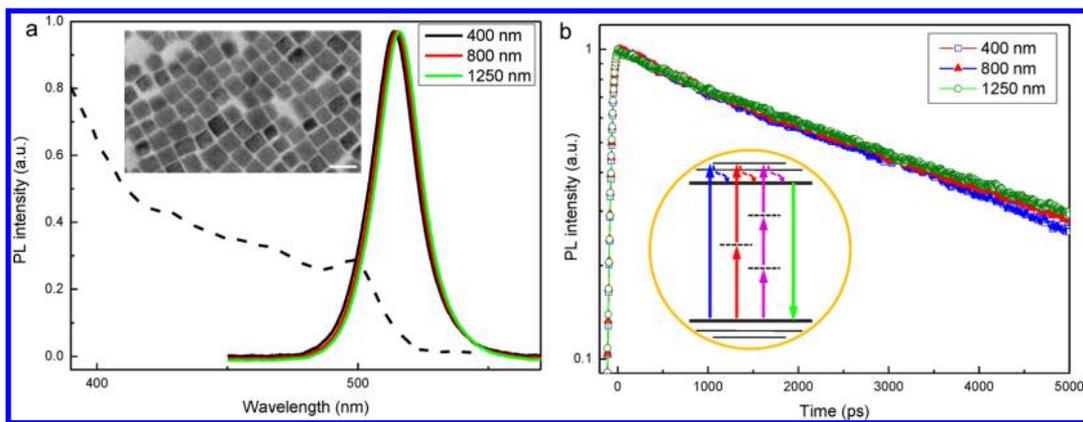


Figure 1. (a) Linear absorption spectrum and one-, two-, and three-photon excited PL spectra from solution of CsPbBr₃ nanocrystals. The inset shows the corresponding TEM image; the scale bar is 20 nm. (b) PL decay traces of CsPbBr₃ nanocrystals based on one-, two-, and three-photon excitation. The inset illustrates the whole process of one-, two-, and three-photon excited PL for CsPbBr₃ nanocrystals.

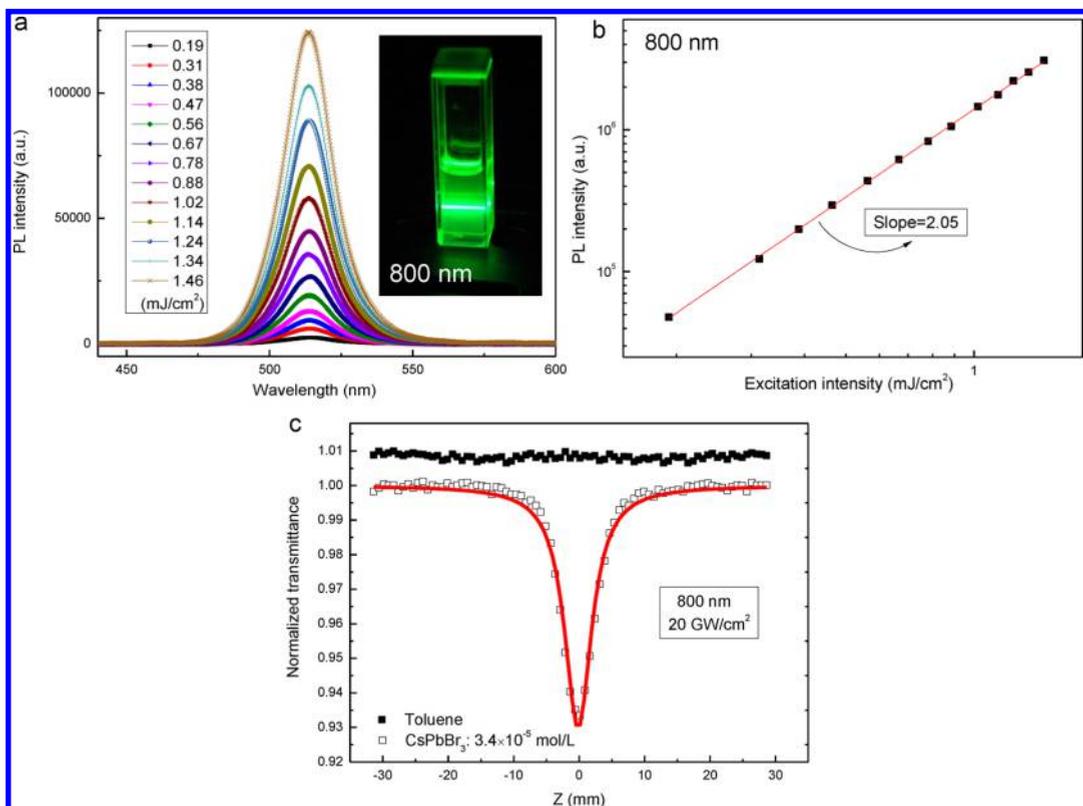


Figure 2. (a) Excitation intensity dependent PL from CsPbBr₃ nanocrystals. The inset shows the photograph of solution of CsPbBr₃ nanocrystals when 800 nm laser beam passed through. (b) Plot of spectrally integrated PL intensity as a function of excitation intensity from CsPbBr₃ nanocrystals. (c) Open aperture Z-scan responses of CsPbBr₃ nanocrystal solution and the pure solvent. The red curve is the best-fitting curve according to Z-scan theory.

achieved by the simple mixing-induced anion exchange at room temperature.^{23–25} Subsequently, the favorable optical gain and lasing attributes of these perovskite nanocrystals were demonstrated by our group and Kovalenko's group, respectively.^{26,27} Simultaneously, the electrically driven LEDs based on these inorganic perovskite nanocrystals were demonstrated by Zeng's group.²⁸

In this work, we, for the first time, investigate the nonlinear optical properties of these emerging CsPbX₃ nanocrystals, which would be of importance for both fundamental physics interest and practical applications.²⁹ We found that the CsPbBr₃ nanocrystals exhibit strong nonlinear absorption and

emission, and a two-photon absorption cross-section as high as $\sim 1.2 \times 10^5$ GM at 800 nm was determined for the 9 nm-sized CsPbBr₃ nanocrystals. Furthermore, low threshold frequency-upconverted stimulated emission from the close-packed thin films of the CsPbBr₃ nanocrystals pumped by simultaneous two- and three-photon absorption was observed. The stimulated emission is favorably stable, and the wavelength could be easily tuned by halide substitution. Our results reveal that the emerging CsPbX₃ nanocrystals are preferred nonlinear optical materials and multiphoton pumped optical gain media, which would provide a new platform in nonlinear photonics and renovate nonlinear devices.

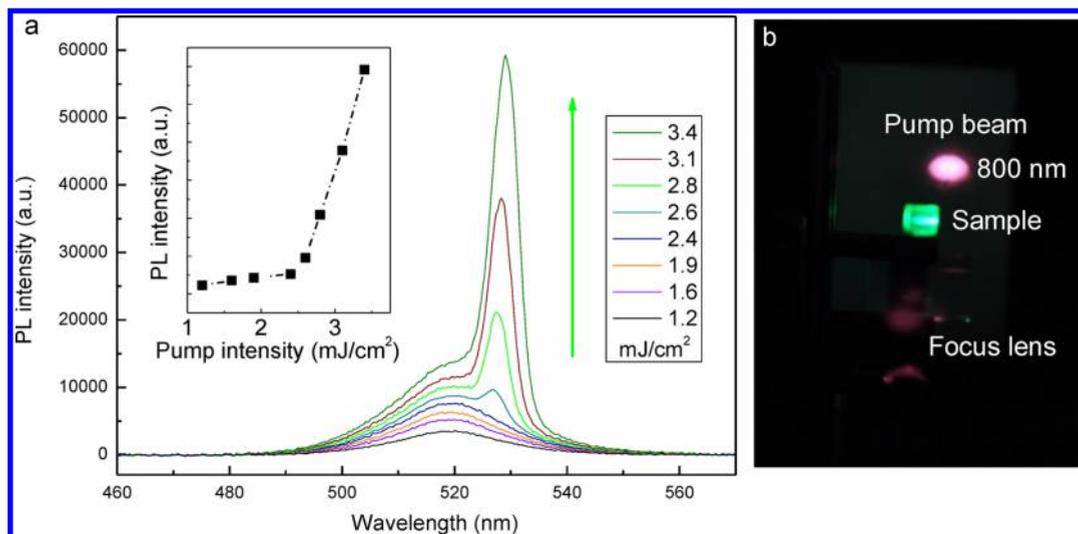


Figure 3. (a) Pump intensity dependent frequency-upconverted PL spectra from thin film of CsPbBr₃ nanocrystals under excitation wavelength of 800 nm. The inset shows the plot of PL intensity as a function of pump intensity. (b) Photograph of the stripe pumping configuration adopted here. The pump beam was focused by a cylindrical lens into a stripe and passed through the sample. A white paper was used to better show the 800 nm pump beam.

The CsPbX₃ nanocrystals investigated here were synthesized following a recipe reported by Protesescu et al. with slight modification.²³ Detailed fabrication process can be found in ref 26. The transmission electron microscope (TEM) image (inset of Figure 1) illustrates the cubic shape of the CsPbBr₃ nanocrystals with an edge length of ~ 9 nm. Figure 1a shows the linear absorption spectrum of CsPbBr₃ nanocrystals in solution, where the linear absorbance is negligible from wavelength longer than ~ 520 nm. However, when 800 nm laser beam passed through the solution of CsPbBr₃ nanocrystals, bright green emission was observed as displayed in the inset in Figure 2a, indicating that the CsPbBr₃ nanocrystals are indeed multiphoton active. The PL spectra from CsPbBr₃ nanocrystals in solution excited by optical wavelength of 400, 800, and 1250 nm, which correspond to one-, two-, and three-photon excitation, respectively, are shown in Figure 1a. To further verify the two- and three-photon absorption and emission process in these CsPbBr₃ nanocrystals, we performed the excitation intensity dependent PL measurement at optical wavelengths of 800 and 1250 nm. As shown in Figure 2b and Figure S1, the quadratic and cubic dependence of the spectrally integrated PL intensity on the excitation intensity clearly confirms the two- and three-photon absorption and emission process under excitation wavelength of 800 and 1250 nm, respectively.^{9,29} It is found that the PL spectra induced by one-, two-, and three-photon absorption are nearly identical. The slight red-shift of two- and three-photon excited PL spectra with respect to that of one-photon counterpart can be attributed to the size inhomogeneity and reabsorption effect,^{9,30} which has been commonly observed in traditional semiconductor quantum dots (QDs).³¹ To gain more insight into the photocarriers, the dynamics based on one (400 nm), two (800 nm), and three-photon (1250 nm) excitation are probed. Figure 1b presents the PL decay curves of CsPbBr₃ nanocrystals, which shows that the decay traces for all of the three excitation mechanisms are almost the same. According to the above results, we can come to the conclusion that the photocarriers excited by either linear absorption or simultaneous two- and three-photon absorption through virtual states

will relax to the same lowest excited state where the radiative recombination (spontaneous emission) occurs. The whole PL processes are schematically illustrated in the inset of Figure 1b.

To quantitatively determine the two-photon absorption cross section of the CsPbBr₃ nanocrystals, the Z-scan measurement was carried out (see experimental details in Experimental Section).^{30,32} The calibration of our Z-scan system was performed by using the liquid carbon disulfide as a reference.^{9,29} Figure 2c displays the Z-scan response of the solution of CsPbBr₃ nanocrystals with concentration of $\sim 3.4 \times 10^{-5}$ mol/L as determined by the inductively coupled plasma atomic absorption spectroscopy (ICP-AAS) (see Experimental Section) and that of the pure solvent (toluene) under input intensity of 20 GW/cm² at optical wavelength of 800 nm. The flat Z-scan curve of the toluene suggests that the nonlinear absorption of the solvent is negligible and that the deep groove response in the Z-scan curve of CsPbBr₃ nanocrystal solution, corresponding to the signal of nonlinear absorption, completely originates from the CsPbBr₃ nanocrystals.²⁹ By fitting the nonlinear absorption response curve based on Z-scan theory, the two-photon absorption coefficient of the CsPbBr₃ nanocrystal solution is derived to be ~ 0.097 cm/GW.^{11,32} Correspondingly, the two-photon absorption cross-section (σ_2) of these CsPbBr₃ nanocrystals is estimated to be 1.2×10^5 GM, which is nearly two-order of magnitude higher than those of conventional green-emitting metal-chalcogenide QDs and comparable to or even larger than those of the best large-sized red-emitting ones.^{9,11,20,33} The high two-photon absorption cross-section observed for these CsPbBr₃ perovskite nanocrystals may be attributed to the relatively large dot size and the intrinsic strong two-photon absorption of lead halide perovskite.^{12,33,34} Such a large two-photon absorption cross-section of these all-inorganic perovskite nanocrystals makes them potential candidates as nonlinear absorbers and related nonlinear photonic media.

Inspired by the strong two-photon absorption and two-photon excited spontaneous emission from these CsPbBr₃ nanocrystals, we attempt to explore the two-photon pumped stimulated emission from these nanocrystals. In doing so, the

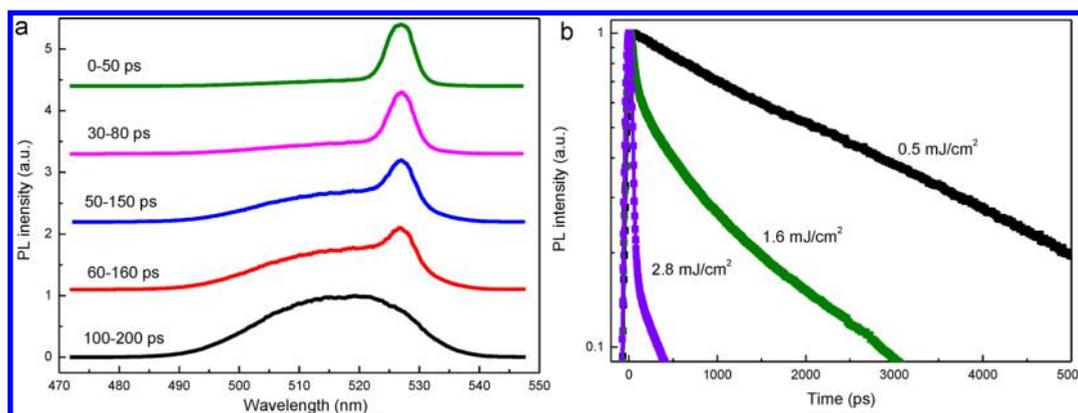


Figure 4. (a) Time-resolved PL spectra from the thin film of CsPbBr₃ nanocrystals under pumping intensity of ~ 2.7 mJ cm⁻². (b) PL decay curves from CsPbBr₃ nanocrystal thin film under varied excitation intensities.

CsPbBr₃ nanocrystals were drop-casted onto a glass substrate, and then, a close-packed solid thin film with thickness of ~ 5 μ m as determined by scanning electron microscopy (SEM) (Figure S2) was obtained. To pump the sample, a 800 nm laser beam with pulse width of 100 fs and repetition rate of 1000 Hz was focused onto the thin film by a cylindrical lens (focus length: 75 mm) with dimension of ~ 100 μ m \times 5 mm to form the stripe pumping configuration, which is favorable to develop stimulated emission thanks to the waveguide effect (see Figure 3b).^{14,27} The PL signal collected from the edge of the sample was dispersed by a 320 mm monochromator and detected by a silicon charged coupled device (CCD). Figure 3a shows the PL spectra from the thin film of CsPbBr₃ nanocrystals under varied pumping intensities. It is found that, under relatively low excitation intensities ($< \sim 2.5$ mJ cm⁻²), the PL spectra are dictated by the broad spontaneous emission with full width at half-maximum (fwhm) of ~ 22 nm. Strikingly, with the further increase of pumping intensity, a new narrow peak emerges, indicating the achievement of frequency-upconverted stimulated emission by two-photon absorption.⁹ The plot of spectrally integrated PL intensity over the narrow peak as a function of pumping intensity exhibits abrupt rising from certain point, further suggesting the development of two-photon pumped stimulated emission from CsPbBr₃ nanocrystals.¹⁵ The spectral position of the new peak with respect to spontaneous emission is analogous to that under one-photon pumping,²⁶ which suggests that two-photon induced stimulated emission is similarly originated from the biexcitonic recombination.^{13,26} The stimulated emission threshold is derived to be as low as 2.5 mJ cm⁻², which stands several times lower than those of the state-of-art red-emitting CdSe-based QDs and may be attributed to the large two-photon absorption cross-section of these CsPbBr₃ nanocrystals.^{9,20,35} Based on the equation $\langle N \rangle = f^2 \sigma_2 / \tau$,³⁵ where f is the pump fluence (photons/cm²) and τ is the pulse width, the average number of excitons per nanocrystal at stimulated emission threshold is estimated to be ~ 1.2 , which agrees well with the biexcitonic stimulated emission mechanism.¹³ To further study the two-photon induced PL dynamics of CsPbBr₃ nanocrystals under different excitation intensities, the time-resolved PL measurements under excitation wavelength of 800 nm was performed using a streak camera system. Figure 4a displays the time-resolved PL spectra from the thin film of CsPbBr₃ nanocrystals under pumping intensity of ~ 2.7 mJ cm⁻², which stays just above the threshold. It can be seen that the narrow stimulated emission peak dominates the PL spectra just after photoexcitation. However, it decays much

faster than the corresponding broad spontaneous emission, which is consistent with the signature of stimulated emission.^{8,9} Finally, the spontaneous emission dominates the PL spectra for long delay times. Figure 4b illustrates the spectrally integrated PL decay curves from CsPbBr₃ nanocrystal thin film under varied excitation intensities spanning from spontaneous emission to stimulated emission. For excitation intensity of far below the threshold, the PL decay trace follows the single exponential decay, corresponding to the single exciton recombination. With increase of excitation intensity, a fast decay path appears, which relates to the multiexciton Auger recombination. When the pumping intensity exceeds the threshold, the PL decay suddenly collapses into < 50 ps, featuring the ultrafast stimulated emission process (see Figure S3 for spectrograms and the corresponding analysis in the Supporting Information). The precise determination of the stimulated emission time scale is hindered by the temporal resolution of our streak camera system (~ 50 ps). As a result, both the time-integrated and time-resolved spectroscopy studies indicate that the frequency-upconverted stimulated emission could be successfully achieved from these CsPbBr₃ nanocrystals by direct two-photon absorption with a low threshold.

An important character of an optical gain material is the photostability under pumping laser irradiation.^{9,22} To access the photostability of our CsPbBr₃ nanocrystal thin film by two-photon pumping, the stimulated emission peak intensity was monitored as a function of pump laser pulses at 800 nm. As shown in Figure 5a, the stimulated emission peak intensity could be readily sustained over more than 6×10^6 uninterrupted laser shots (~ 1.7 h), which is nearly three-order of magnitude longer than that of traditional two-photon pumped dyes and comparable to those of semiconductor quantum dots.^{22,36}

Having manifesting the stimulated emission by two-photon absorption from the thin film of CsPbBr₃ nanocrystals, we move forward to investigate the three-photon pumped stimulated emission, which could offer even greater advantages over the two-photon analogues.^{9,21} In order to observe the stimulated emission by simultaneous three-photon absorption, the favorable stripe pumping configuration was again employed. Figure 5b displays the pumping intensity dependent PL spectra from the CsPbBr₃ nanocrystal thin film under excitation wavelength of 1250 nm. The appearance of narrow peak under high excitation intensities and the threshold behavior of the plot of the integrated PL intensity over the narrow peak with

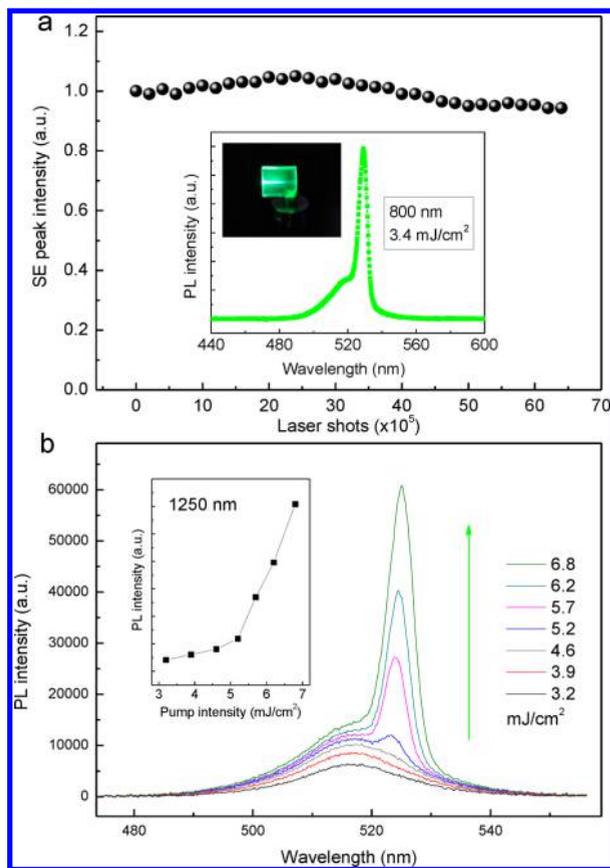


Figure 5. (a) Plot of stimulated emission peak intensity versus pump laser shot. The inset displays the PL spectrum and the photograph of the sample under excitation of focused 800 nm laser beam with pumping intensity of 3.4 mJ/cm². (b) Three-photon pumped PL spectra from CsPbBr₃ nanocrystals under excitation wavelength of 1250 nm and varied pump intensities. The inset shows the plot of corresponding integrated PL intensity as a function of pump intensity.

respect to excitation intensity unambiguously establish the development of three-photon pumped stimulated emission from these CsPbBr₃ nanocrystals.⁹ The stimulated emission threshold (~ 5.2 mJ/cm²) is found to be even lower than that of deliberately designed CdSe/CdS/ZnS core/multishell QDs emitting in red spectral range.⁹ It should be noted that the stimulated emission in green region from semiconductor QDs by direct three-photon pumping has not yet been observed until now, which is mainly ascribed to the smaller multiphoton absorption cross sections and the faster nonradiative Auger recombination for the traditional green-emitting QDs than those of red-emitting ones.^{9,15} Our result represents the first realization of three-photon pumped green stimulated emission from colloidal QDs, which may offer new possibilities in biophotonics.⁹

In previous work, we have demonstrated the facile stimulated emission tunability by changing the halide composition under one-photon pumping.²⁶ However, the threshold is found to increase when substituting the Br by Cl or I for wavelength tailoring, which might be attributed to the increased carrier trapping defects in the halide-mixed nanocrystals.^{26,27} Since the multiphoton pumped stimulated emission threshold is typically orders of magnitude higher than that of one-photon counterpart,⁹ the increased carrier trapping loss may lead to photodamaging the sample before the achievement of

frequency-upconverted stimulated emission in the halide-mixed nanocrystals. Therefore, it is significant to investigate the feasibility of wavelength-tunable stimulated emission from these perovskite nanocrystals based on two-photon pumping. To this end, we gradually augment the ratio of Cl/Br in CsPb(Cl/Br)₃ nanocrystals so that the spontaneous emission peak keeps blue-shifted. By following the same thin film preparation method and pumping configuration for these halide-mixed nanocrystals as mentioned above, we observed the two-photon pumped stimulated emission from these perovskite nanocrystals with wavelength tunable by halide substitution as shown in Figure S4. The realization of two-photon pumped low threshold, photostable, and wavelength tunable stimulated emission in these perovskite nanocrystals indicates that the emerging perovskite nanocrystals are favorable frequency-upconverted optical gain media.

In conclusion, we have investigated the nonlinear absorption and emission properties of the emerging all-inorganic CsPbBr₃ nanocrystals. A large two-photon absorption cross-section of up to $\sim 1.2 \times 10^5$ GM is determined for 9 nm sized CsPbBr₃ nanocrystals. Low-threshold, photostable, and wavelength tunable frequency-upconverted stimulated emission by two-photon absorption was observed from these CsPb(Cl/Br)₃ nanocrystals. For the first time, we realize the three-photon pumped green stimulated emission from colloidal nanocrystals. Our results reveal that the newly emerging CsPbX₃ perovskite nanocrystals are attractive frequency-upconverted optical gain media, which may provide new opportunities for nonlinear photonics.

Experimental Section. Mole Concentration Determination of CsPbBr₃ Nanocrystals. The mole concentration of CsPbBr₃ nanocrystals are determined by the inductively coupled plasma atomic absorption spectroscopy (ICP-AAS, IRIS Intrepid II XSP, Thermo Electron, USA). First of all, 10 μ L of the nanocrystal dispersion was diluted with 2 mL of toluene. Then, concentrated nitric acid (40%, vol.) and distilled water were added into above dispersion to form a nitric acid solution (8%, vol.). The solution was shaken on a shaker for 2 days to dissolve the ions thoroughly. After standing, 10 mL of the lower solution was taken out for ICP-AAS measurement, and the concentration was decided from the result of lead.

Optical Measurements. A femtosecond amplified-pulsed laser system was adopted as the laser source. The output wavelength can be continuously tuned from 250 nm to 2.6 μ m through an optical parameter amplifier. The pulse-width and repetition rate are 100 fs and 1 kHz, respectively. For the Z-scan measurements, the laser beam was divided into two parts by a beam splitter. One acted as the reference, and the other one was focused onto the 1 mm thick quartz cuvette filled with solution of CsPbBr₃ nanocrystals by a circular lens (focus length: 20 cm) and detected by a Si biased detector equipped with standard lock-in amplifier technique. The sample was controlled by a step motor to travel along the laser beam back and forth. In doing the time-resolved PL measurements, the solution of CsPbBr₃ nanocrystals was filled into a quartz cuvette with thickness of 1 mm. The backscattering configuration was employed to collect the PL signal by an Optronis streak camera system. For the measurement of dynamics of thin films of CsPbBr₃ nanocrystals, the PL signals were vertically collected from the edge of the sample and analyzed by the Optronis streak camera system with temporal resolution of ~ 50 ps.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.5b04110.

Detailed information on the scanning electron microscopy (SEM) characterization of thin film of CsPbBr₃ nanocrystals, time-resolved spectrograms of CsPbBr₃ nanocrystals under two-photon excitation, and the wavelength-tunable frequency-upconverted stimulated emission from halide-mixed CsPb(Cl/Br)₃ nanocrystals (PDF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

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