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Efficient up-conversion photoluminescence in all-inorganic lead halide perovskite nanocrystals

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ABSTRACT

Up-conversion photoluminescence (UCPL) refers to the elementary process where low-energy photons are converted into high-energy ones via consecutive interactions inside a medium. When additional energy is provided by internal thermal energy in the form of lattice vibrations (phonons), the process is called phonon-assisted UCPL. Here, we report the exceptionally large phonon-assisted energy gain of up to $\sim 8k_B T$ (k_B is Boltzmann constant, T is temperature) on all-inorganic lead halide perovskite semiconductor colloidal nanocrystals that goes beyond the maximum capability of only harvesting optical phonon modes. By systematic optical study in combination with a statistical probability model, we explained the nontrivial phonon-assisted UCPL process in perovskites nanocrystals, where in addition to the strong electron-phonon (light-matter) coupling, other nonlinear processes such as phonon-phonon (matter-matter) interaction also effectively boosts the up-conversion efficiency.

KEYWORDS

up-conversion photoluminescence, phonons, lead halide perovskite, colloidal nanocrystals

1. Introduction

Light up-conversion is a fundamental process, through which a medium converts low-energy into high-energy photons after sequential absorption events. While light emission usually occurs at energies below photoexcitation, spontaneous up-conversion photoluminescence (UCPL) occurs at above the excitation energy under energy-conservation mechanisms but with much lower efficiency [1, 2]. First, an excitation photon ($\hbar\omega_{\text{Exc}}$) couples to an intermediate (real or virtual) state and eventually produces PL at higher energy ($\hbar\omega_{\text{Det}}$) from the real electronic level $|X\rangle$ after acquiring an additional energy of $-\Delta E = \hbar\omega_{\text{Det}} - \hbar\omega_{\text{Exc}}$ (see Fig. 1(a)). In solid-state systems, if $|\Delta E|$ is provided by internal thermal energy (U_{Int}) in the form of lattice vibrations (phonons), the phenomenon is called phonon-assisted UCPL, which must be distinguished from other non-linear optical phenomena such as two-photon absorption (TPA) or second harmonic generation (SHG) [3, 4]. Light up-conversion has been demonstrated in several systems, such as rare-earth-doped materials [5-8], organic dyes [9-11], carbon nanotubes [12], II-VI nanobelts [13, 14], colloidal semiconductor nanocrystals (NCs) [15-19] and lead halide perovskites [20], for a variety of applications such as biomedical imaging, frequency up-converted lasing, efficient photovoltaics and optical refrigeration.

The past decade has witnessed tremendous attention on lead halide semiconductors with a perovskite crystal structure (see Fig. 1(b)) for light-harvesting and light-emitting applications [21-27]. Their excellent optical properties arise from the direct-bandgap nature and large absorption coefficients. Along with the development of the bulk counterpart, all-inorganic perovskite NCs have been also reported [28]. This class of colloidal NCs exhibits high quantum-yield of up to $\sim 90\%$, strong and tunable luminescence over the entire visible region of the electromagnetic spectrum, by varying sizes and compositions [28-30]. Therefore, colloidal perovskite NCs offer new platforms for tailoring the energy spectra of excitons (coupled electron-hole pairs), which are responsible for the optical responses. More interestingly, perovskite semiconductors exhibit strong UCPL signals. However, there is still a lack of complete understanding on how much thermal energy can be exploited for up-converting light, especially in this new material family.

In this work, we present a systematic study on the light up-conversion properties of a set of high-quality all-inorganic CsPbA_3 ($A = \text{I, Br, Cl, I:Br and Br:Cl}$) perovskite semiconductor colloidal NCs. Surprisingly, we find an efficient up-conversion luminescence with striking phonon-assisted energy gain of up to 200 meV ($\sim 8k_B T$) at room temperature, which is an order of

magnitude larger than the maximum energy can be converted via direct electron-optical phonon coupling. The deficiency of phonon population after few absorption events limits the probability of the next absorption. Therefore, the acoustic phonon quasi-continuum is needed to refill the optical phonon bath. This so-called phonon up-conversion is especially strong in materials having low thermal conductivity such as lead halide perovskites. Our work may be beneficial for the future design of nanomaterials for energy-harvesting devices and quantum optical refrigeration.

Figure 1. Up-conversion photoluminescence in perovskite nanocrystals. (a) Schematic diagram for phonon-assisted UCPL, which occurs by absorption of one photon energy $\hbar\omega_{\text{Exc}}$ (orange arrow) and subsequently internal energy U_{Int} (wavy arrow). The created exciton at $|X\rangle$ -state radiatively recombines yielding a photon with energy of $\hbar\omega_{\text{Det}} \geq \hbar\omega_{\text{Exc}}$ (blue arrow). ΔE is defined as $\Delta E = \hbar\omega_{\text{Exc}} - \hbar\omega_{\text{Det}}$. (b) Crystal structure of CsPbA₃ perovskites, in which, Cs⁺ is located within the cages formed by octahedral coordination of Pb²⁺ and A⁻.

2. Results and discussion

2.1. Sample characterization and optical properties

Caesium lead halide NCs were prepared using the solution-phase synthesis methodology reported by Protesescu *et al.* [28] (see Methods section). CsPbA₃ NCs were intensively characterized by transmission electron microscopy (TEM) and optical spectroscopy. Most of the synthesized CsPbA₃ nanostructures have cubic-like shape with typical lateral sizes (L) of ~ 10 nm and surface area of $S = L^2 \sim 100$ nm². Figure 2(a) shows a representative TEM image of CsPbBr₃ NCs, which have an average size of $\langle L \rangle = (9.9 \pm 2.3)$ nm. The diffraction planes are clearly revealed in the high-resolution TEM image (see Fig. 2(b)) indicative of the high crystallinity. The CsPbA₃ NCs ensembles were prepared by solution spin-coating on cleaned SiO₂/Si substrates for photoluminescence (PL) experiments with varying excitation energy, power and temperature.

Figure 2(c) shows normalized room-temperature PL spectra for perovskite NCs with different compositions. PL emission of iodide based NCs (red solid curve) takes place in the red region of the electromagnetic spectrum (~ 1.8 eV). The PL spectral position shifts to ~ 2.4 eV and to ~ 3.1 eV when using Br (green solid curve) or Cl (violet solid curve) atoms, respectively. The emission energy can be further manipulated, not only by varying the NC size [28], but also by alloying the halide elements to cover the entire visible region. For instance, the mixture I:Br leads to the orange spectrum centered at ~ 2.2 eV, while Br:Cl results in the light-blue and dark-blue spectra located at ~ 2.6 eV and ~ 2.7 eV, respectively. The exact energy position of the alloyed NCs depends on the precise stoichiometric ratio of the halides. The relatively narrow PL linewidths of 80-100 meV for CsPbA₃ NCs

are comparable to those reported for perovskite NCs [28, 29, 31-33] and traditional II-VI quantum dots [34-36].

Figure 2(d) shows room-temperature PL decay curves for CsPbI₃ (red curve), CsPbI_{1.5}Br_{1.5} (orange curve), CsPbBr₃ (green curve) and CsPbBr₂Cl (blue solid curve) NCs under 3.1 eV excitation. The transient spectra show multi-exponential

Figure 2. Sample characterization and optical properties. (a) Representative TEM image of CsPbBr₃ NCs showing the cubic-like shape with average lateral side of $\langle L \rangle \sim 9.9$ nm (inset). (b) High-resolution TEM image showing clear diffraction planes of the crystalline NCs. (c) Normalized PL spectra taken at $T = 296$ K of CsPbI₃ (red solid line), CsPbI_{1.5}Br_{1.5} (orange solid line), CsPbBr₃ (green solid line), CsPbBr₂Cl (light-blue solid line), CsPbBr_{1.5}Cl_{1.5} (dark-blue solid line) and CsPbCl₃ (violet solid line). Normalized linear absorption spectra taken at $T = 296$ K are given for CsPbI₃ (red dashed line) and CsPbCl₃ (violet dashed line). The inset shows an optical image of the perovskite NC solutions under illumination of UV light. (d) Room-temperature PL decay curves for CsPbA₃ NCs on a semi-logarithmic scale. The time-resolved spectra are labelled by the corresponding constituent halide atoms. The black solid lines are biexponential fitting curves. Inset: Average PL decay time $\langle \tau \rangle$ is shown for the investigated NCs as a function of the emission energy.

behaviors as typically observed in semiconductor NCs [33, 37, 38]. In our case, we model the PL decay curves by biexponential functions (black lines). The obtained PL lifetimes τ_1 and τ_2 are listed in Table S1. The faster decay component τ_1 is ~ 26 ns for CsPbI₃ and decreases to ~ 11 ns for CsPbBr₂Cl that are in good agreement with literature [28, 33]. Furthermore, we report a long PL lifetime $\tau_2 \sim 90$ ns for all compounds, but its contribution to the total PL decay varies with compositions. In NCs, long decay channels are normally attributed to forbidden (dark) transitions, originating from dark exciton recombination.

Further experiments by monitoring temperature dependence or magnetic fields of the PL decays are required to elucidate the precise nature of these emitting channels.

An intensity-averaged decay time $\langle \tau \rangle = \sum_i C_i \tau_i / \sum_i C_i$ is shown as a function of the emission energy of each NCs (see inset), where C_i ($i = 1, 2$) is the amplitude of each PL decay component i . The major contribution of the long PL decay channels (C_1, C_2) to the total light emission and the absence of low-energy and poorly emitting defect bands in the PL spectra (see Fig. S4 in the ESM) of the NCs confirms the high quality of our samples.

2.2. Up-conversion luminescence with varying excitation energy, power and temperature

Figure 3(a) shows room-temperature linear absorption (black line) and photoluminescence (blue line) spectra of CsPbBr₃ NCs as a representative system to discuss the UCPL in perovskite NCs. The PL spectrum centered at $\hbar\omega_{\text{Det}} \sim 2.4$ eV is monitored while varying the excitation wavelength (color-coded arrows). Figure 3(b) compares the room-temperature luminescence spectrum under 2.71 eV excitation ($\lambda_{\text{Exc}} = 457$ nm, blue curve) with up-conversion spectra taken with laser energies of 2.33 eV ($\lambda_{\text{Exc}} = 532$ nm, green curve), 2.20 eV ($\lambda_{\text{Exc}} = 564$ nm, orange curve) and 1.96 eV ($\lambda_{\text{Exc}} = 633$ nm, red curve). Although the absorption at these energies is negligible, the up-conversion signal remains strong. Importantly, all spectra exhibit similar peak positions and linewidths, confirming that the luminescence signal originates from the same subset of NCs, in contrast to the observation in II-VI (e.g., CdSe, CdTe) NCs [15, 39] (see also Fig. S1 in the Electronic Supplementary Material (ESM)).

Figure 3. UCPL versus excitation energy, power and temperature. (a) Linear absorption (black curve) profile of CsPbBr₃ NCs at $T = 296$ K. The color-coded arrows denote the used excitation energies ($\hbar\omega_{\text{Exc}}$) in the UCPL experiments. $\hbar\omega_{\text{Det}}$ denotes the PL center energy (blue curve). (b) Normalized room-temperature UCPL spectra of CsPbBr₃ NCs under excitation energies of 2.71 eV (blue curve), 2.33 eV (green curve), 2.20 eV (orange curve) and 1.96 eV (red curve). (c) Power-dependent UCPL spectra of CsPbBr₃ NCs at $T = 296$ K under 2.33 eV excitation photon energies. The maximum power density is $P_0 = 1.6$ kWcm⁻². (d) UCPL spectra under 2.33 eV excitation taken at $T = 80$ K (red curve) and $T = 296$ K (blue curve) using the same power density. The UCPL intensity decreases with decreasing temperature.

For each excitation energy, the PL signal was studied as a function of power (P) of continuous laser excitation and temperature (T). Figure 3(c) shows typical room-temperature UCPL spectra obtained with 2.33 eV excitation. The laser power was initially $P_0 = 1.6$ kWcm⁻² and varied across two orders of magnitude, leading to a linear drop of emission intensity. This behavior suggests that only one photon participates in the up-conversion process. Keeping the same photoexcitation energy and power density while decreasing temperature from 296 K (blue curve, Fig. 3(d)) to 80 K (red curve), the spectrum shifts to lower energy as normally observed in these perovskite materials [40-43]. Furthermore, the decreasing intensity at lower temperature strongly suggests the critical role of the NC thermal energy in the UCPL process.

2.3. Power-dependence and temperature-dependence

The detailed power-dependence of the integrated PL intensity (I) at room temperature for CsPbBr₃ NCs is shown in Fig. 4(a) in a log-log scale for all the used laser wavelengths. The intensity I is fitted to the power law $I = \alpha P^\beta$ (colored solid lines), where P is power density in the excitation area (12 μm^2). Excitation above the NC bandgap (i.e., $\hbar\omega_{\text{Exc}} \geq \hbar\omega_{\text{Det}} = 2.41$ eV, PL regime) leads to a sublinear ($\beta \leq 1$) power-dependence, which is typical for quantum systems [19, 44]. Below-bandgap excitation (i.e., $\hbar\omega_{\text{Exc}} < \hbar\omega_{\text{Det}}$, UCPL regime), where linear absorption is weak or negligible, the intensity decreases drastically with decreasing excitation energy and remains sublinear till $\hbar\omega_{\text{Exc}} = 2.20$ eV. At around $\hbar\omega_{\text{Exc}} = 2.15$ eV, the intensity saturates, and the slope becomes steeper with $\beta \sim 2$. Sublinear power-dependence suggests that the UCPL is governed by absorption of one-photon followed by absorbing NC thermal energy, whereas, the superlinear power-dependence ($\beta \sim 2$) implies two-photon absorption process (see also Fig. S2 in the ESM). This is further confirmed by the temperature-dependent PL at various laser energies.

Figure 4(b) shows the normalized prefactor α as a function of temperature. Two distinct trends are clearly observed. For the process merely involving the absorption of photons ($\hbar\omega_{\text{Exc}} = 2.71$ eV and 1.96 eV) by either one- (blue diamonds) or two-photon (red squares), α monotonically increases with decreasing temperature. This increment is due to the higher quantum-yield at lower temperature as normally observed in NCs [37]. On the other hand, for the processes requiring absorption of NC thermal energy, the UCPL weakens with decreasing temperature (green circles). With the excitation at 2.20 eV, α exhibits a dual behavior (orange triangles) alike a temperature-induced switch of the fluorescence mechanism, which defines the room-temperature energy threshold between phonon-assisted up-conversion and two-photon absorption in CsPbBr₃ NCs. The experimental results at room temperature are summarized in Fig. 4(c) for different compounds. The power exponent β is depicted as a function of energy difference ΔE . The step-like behavior of β clearly delimits different mechanisms at room temperature, where phonon-assisted regime occurs in an energy window from 0 to 250 meV and the multiple-photon absorption process takes place beyond 250 meV. The surprisingly large threshold of ~ 200 meV is independent of NC compositions and surpasses that of other semiconductors NCs [15, 39, 45].

Figure 4. Energy gain for phonon-assisted UCPL. (a) Power dependence of the integrated intensity (I) after photo-excitation at 2.71 eV (blue diamonds), 2.33 eV (green circles), 2.20 eV (orange down-triangles), 2.15 eV (light-green stars) and 1.96 eV (red squares). The colored solid lines are fittings to the power law $I = \alpha P^\beta$. The black dashed line represents $\beta = 1$. (b) Temperature dependence of pre-factor α for the used excitation energies in (a) with the same symbol and color convention. α has been normalized to the maximum value α_{Max} of each $\hbar\omega_{\text{Exc}}$ for comparison. The colored dashed lines are guidelines. (c) Extracted room-temperature β for all the investigated CsPbA₃ NCs as a function of ΔE . The chemical compositions are indicated by the legends. The clear switch between one- and two-photon absorption occurs at $\Delta E \sim 200$ meV. (d) Room-temperature Raman spectrum of CsPbBr₃, showing the LO phonon energy of 16 meV.

In order to understand the efficient phonon-assisted UCPL in perovskite NCs, knowledge of the phonon spectrum is crucial. A non-resonant Raman spectrum of CsPbBr₃ taken at room temperature using 1.96-eV excitation (see Fig. 4(d)) exhibits a number of sharp features at energies below ~ 20 meV: two sets of doublets centered at ~ 5 meV and ~ 10 meV and a broader structure at ~ 16 meV. The spectral positions of the Raman signals are in good agreement with experiments [46, 47] and calculations [48], from which, we identify an optical phonon mode at ~ 16 meV. At high-energy region of ~ 200 meV, no phonon modes were detected. The lack of lattice vibrations matching with the large energy gain of ~ 200 meV reveals that multiple phonon-assisted UCPL events have to take place with high efficiency.

2.4. Electron-phonon interaction in CsPbA₃ NCs

We employed transient absorption (TA) spectroscopy to study the carrier relaxation in CsPbA₃ NCs, which provides the timescale for electron-phonon interactions. Figure 5(a) shows a typical TA map obtained for CsPbBr₃ NCs at room temperature. The used pump-fluence was $35.7 \mu\text{J}/\text{cm}^2$, producing an average number of excited carriers per NC, $\langle N \rangle \sim 1$ (see Extended Discussion, Section 1 in the ESM). A pronounced bleaching feature (positive $\Delta T/T$) appears at the optical bandgap (~ 2.5 eV). At early delay time, the bleaching exhibits a considerable

broadening in the high-energy side and gets narrower afterwards that indicates the existence of hot carrier. A pump-induced absorption (PIA) feature (negative $\Delta T/T$) at the high-energy side is assigned to the excited-state absorption, while the PIA at low-energy side arises from the exciton-exciton (biexciton) interaction [33, 49, 50].

The extracted transient transmission spectra at selected time delay from 0.2 to 10 ps are shown in Fig. 5(b). The high-energy tail of the bleaching feature can be well fitted by the Maxwell-Boltzmann distribution $\Delta T/T \propto \exp(-E/k_B T_c)$ (black dashed lines) to obtain the effective electronic temperature T_c . The representative fitting curves are shown by black lines. The same fitting criteria were used for all the spectra resulting in the decay of carrier temperature as shown in Fig. 5(c). Carriers gets cooled in the first 3 ps, then T_c saturates at longer delay time.

Figure 5. Electron-phonon coupling in CsPbA₃ NCs. (a) Pseudo-color ($\Delta T/T$) representation transient transmission spectra for CsPbBr₃ NCs using excitation energy of 3.82 eV with low pumping fluence. The average number of excited carriers per NC is $\langle N \rangle \sim 1$. The broadening at early time indicates the existence of hot carriers. (b) Normalized transient transmission spectra at selected pump-probe time delays from 0.2 ps to 10 ps (colored solid lines). The high-energy tails are fitted by Boltzmann distribution, as shown by black lines for example. (c) Carrier temperature (blue circles) extracted from (b) as a function of delay time. The carrier cooling is modelled by Eq. (1), resulting an effective cooling time of $\langle \tau_{\text{cooling}} \rangle \sim 1.5$ ps.

In polar semiconductors as lead halide perovskites, the carrier relaxation is governed by the Fröhlich interactions between carriers and longitudinal optical (LO) phonons by elastic scattering. The stronger the interaction is, the faster the relaxation occurs. The carrier-LO coupling strength can be quantified by [48, 51, 52]:

$$-\frac{3k_B}{2} \frac{dT_c}{dt} \approx \frac{\hbar\omega_{\text{LO}}}{\langle \tau_{\text{cooling}} \rangle} \left[\exp\left(-\frac{\hbar\omega_{\text{LO}}}{k_B T_c}\right) - \exp\left(-\frac{\hbar\omega_{\text{LO}}}{k_B T_l}\right) \right] \quad (1)$$

where T_l is the lattice temperature and $\hbar\omega_{\text{LO}} = 16$ meV (see Fig. 4(d)). The cooling dynamic curve can be well fitted to Eq. (1) as shown in Fig. 5(c), with $\langle \tau_{\text{cooling}} \rangle \approx 1.5$ ps. The cooling rate in CsPbBr₃ NCs is slightly slower than II-VI semiconductor NCs [53-56], which are typical systems demonstrating strong Fröhlich interaction [13, 57, 58]. Although the electron-phonon coupling in perovskite NCs is slightly weaker than II-VI NCs, the larger energy gain found in perovskite NCs reveals that electron-phonon interaction is important but not the only factor determining the total UCPL efficiency.

2.5. Statistical probability model

A kinetic three-level energy scheme has been previously

introduced to phenomenologically describe the UCPL dynamics [12, 39] that occurs more efficiently with smaller $|\Delta E|$ and faster electron-phonon coupling rate (see Extended Discussion, Section 2 in the ESM). However, a limitation of this three-level model is that it cannot calculate the maximum thermal energy to be converted into light energy by a solid ($|\Delta E|_{\text{Max}}$). Therefore, we propose an alternative approach aiming to quantify $|\Delta E|_{\text{Max}}$. Our model takes into account n consecutive absorption of LO phonons via n intermediate levels separated by a phonon energy ε_{ph} (see Fig. 6(a)). The intermediate levels, which can be either real or virtual, carry weak or negligible oscillator strengths and therefore, have weak light absorption and emission (see Fig. 2(d) and Fig. S3 in the ESM).

We consider a cubic-like solid with lateral size L and volume $V = L^3$. A low-energy photon $\hbar\omega_{\text{Exc}}$ creates cold carriers at the level $|0\rangle$, which can either elastically scatter back to the ground state $|g\rangle$ or absorb phonons to the upper levels. At the intermediate state $|i\rangle$, which can be either real or virtual, there are three possible pathways: (i) non-radiatively decay to $|g\rangle$ with probability P_i^{NR} , (ii) emit a phonon to state $|i-1\rangle$ with probability P_i^{Em} and (iii) absorb a phonon to $|i+1\rangle$ with probability P_i^{Abs} . To reach the intrinsic electronic state $|X\rangle$ and then emit a high-energy photon, the probability of phonon absorption ($Q_{\uparrow}$) needs to outcompete with the total probability of decay to lower states ($Q_{\downarrow}$) that are expressed as follows:

$$Q_{\uparrow} = \prod_{i=0}^{n-1} P_i^{\text{Abs}} = \prod_{i=0}^{n-1} (N-i)p(\varepsilon_{\text{ph}}; T)\gamma_{\text{e-ph}} \quad (2a)$$

$$Q_{\downarrow} = \prod_{i=0}^{n-1} P_i^{\text{Em}} + \prod_{i=0}^{n-1} P_i^{\text{NR}} = \prod_{i=0}^{n-1} (N+1-i)(p(\varepsilon_{\text{ph}}; T)+1)\gamma_{\text{e-ph}} + \prod_{i=0}^{n-1} \gamma_{\text{NR},i}, \quad (2b)$$

where N is the number of available phonons estimated as $N = (L/L_0)^3$ with typical lattice constant values of $L_0 \sim 0.5$ nm [59]. The term $p(\varepsilon_{\text{ph}}; T) = (\exp(\varepsilon_{\text{ph}}/k_B T) + 1)^{-1}$ is the Bose-Einstein distribution, $\gamma_{\text{e-ph}}$ is the electron-phonon scattering rate and $1/\gamma_{\text{NR},i} = \hbar/2(\hbar\omega_{\text{Det}} - i\varepsilon_{\text{ph}})$, defined by Heisenberg uncertainty, is the annihilation rate of cold carriers at the virtual state $|i\rangle$. After normalization, the probability for multiple phonon absorption events is given as:

$$P_{\uparrow}^{\text{Abs}} = \frac{Q_{\uparrow}}{Q_{\uparrow} + Q_{\downarrow}} \quad (3)$$

As a result of our model, the probability $P_{\uparrow}^{\text{Abs}}$ decreases exponentially with the number of LO absorbed that follows the Bose-Einstein and also agrees with the theory previously proposed in Ref. [60]. The expected energy gain can be estimated as $\langle \Delta E \rangle \sim |E|_{\text{Max}} = \sum_n n\varepsilon_{\text{ph}} P_{\uparrow}^{\text{Abs}}$. Since electrons preferentially couple to LO phonons, whose energy spectrum is discrete, we consider a spacing of $\varepsilon_{\text{ph}} = \hbar\omega_{\text{LO}}$ between intermediate levels. In the calculation, we used experimental parameters of $\hbar\omega_{\text{Det}} = 2.41$ eV (see Fig. 3(b)), $\hbar\omega_{\text{LO}} = 16$ meV (see Fig. 4(d)) and $1/\gamma_{\text{e-ph}} \approx 1/\gamma_{\text{cooling}} \sim 1.5$ ps (see Fig. 5(c)) for CsPbBr₃ NCs and $\hbar\omega_{\text{Det}} = 2.07$ eV [61] and 2.14 eV [16, 17], $\hbar\omega_{\text{LO}} = 21$ meV [62, 63] and 26 meV [64–66], $1/\gamma_{\text{e-ph}} \sim 0.3$ ps [67] and 0.6 ps [54, 56] for CdTe and CdSe NCs, respectively.

The calculated energy gain for several semiconductor NCs is shown in Fig. 6(b) (blue bars). With increasing LO phonon energy, the absorbed thermal energy decreases rapidly following Bose-Einstein distribution that agrees well with experimental trend (orange bars). Quantitatively, the maximum gain $|\Delta E|_{\text{Max}}$ is still smaller than the measured value by an order of magnitude. In a more complicated scenario, when all the states $|i\rangle$ are real arising from defect or trap states, the

annihilation rate $\gamma_{\text{NR},i}$ decreases, leading to an increase of $|E|_{\text{Max}}$. However, when $\gamma_{\text{NR},i}$ is much slower than $\gamma_{\text{e-ph}}$, the energy gain saturates and no longer increases with $\gamma_{\text{NR},i}$. The dependence of $|E|_{\text{Max}}$ on $\gamma_{\text{NR},i}$ is shown in Fig. S7.

Figure 6. Statistical probability model. (a) Schematic of the statistical probability model, considering sequential absorption of n phonons with energy of ε_{ph} . P_i^{Abs} , P_i^{Em} and P_i^{NR} denote the probabilities for absorbing, emitting a phonon and nonradiative relaxation from the intermediate state $|i\rangle$, respectively. (b) Computed maximum energy acquired from LO phonons for UCPL in different semiconductor NCs considering direct carrier-LO coupling only (light-blue bars) and the maximum values obtained in experiments (orange bars).

The large discrepancy between the predicted $|\Delta E|_{\text{Max}}$ and the experimental one reveals that phonon-assisted UCPL requires contribution from not only optical phonons but also other species in the thermal bath. It is also evidenced by the pronounced UCPL signal when the LO phonon population is negligible ($T = 80$ K, Fig. 3(d)). On the other hand, low-energy phonons (~ 1 -3 meV) are still abundant at any temperature. However, the converted lattice energy via acoustic modes is typically few meV [68]. Hence, we expect that the direct electron-acoustic and electron-optical phonon coupling are not sufficient to explain for the up-conversion PL in semiconductor NCs, especially for the energy gain of ~ 200 meV ($\sim 8k_B T$) gain in CsPbA₃ NCs at room temperature.

Different mechanisms have been proposed to explain for the phonon-assisted UCPL in perovskite NCs. Ye *et al.* [69] and Ma *et al.* [70] discussed the possibility of the self-trapped states lying at ~ 30 meV below the NC gap, where cold photo-excited carriers reside and are thermally excited to the intrinsic exciton state. In our case, no self-trapped state is observed in the PL/UCPL spectra. Furthermore, we monitor the emission properties only at the intrinsic exciton state. No energy shift between the PL and UCPL spectra is observed. On the other hand, a comparative study on CsPbBr₃ NCs with and without trap states [71] suggests that the discrete mid-gap states do not contribute significantly to the one-photon UCPL mechanism that is in line with the prediction from our model. By considering intermediate real states in CsPbA₃ NCs, we find that the maximum energy gain increases to ~ 32 meV (see Fig. S7), which is still much smaller than $|E|_{\text{Max}} \sim 200$ meV found in our experiments. We do not exclude the role of self-trapped or defect states on UCPL processes as mentioned in Ref. [69-71]. Indeed, to further enhance the UCPL energy gain toward ~ 200 meV, in addition to the nature of the intermediate states $|i\rangle$ arising from traps/defects, we propose that the one-photon UCPL process requires multiple-LO-phonon absorption and the thermal energy provided by the acoustic phonons via acoustic-to-optical up-conversion should also be considered.

2.6. Discussion

Upon the laser excitation, the photo-created carriers at the intermediate state can directly couple to optical or acoustic modes. At room temperature, both optical and acoustic phonon population are equivalently sizable, leading to high probability of phonon-absorption, while electron-optical coupling dominates. After the first few absorption events, such preferential interaction with the optical phonons leads to the deficiency of optical phonon modes that prevents for further absorption, while the acoustic phonon bath remains almost intact. The resultant non-equilibrium populations activate the phonon up-conversion process, during which, multiple low-energy (acoustic) phonons are annihilated creating a high-energy (optical) vibration [72, 73]. Strong acoustic-acoustic phonon annihilation results in the efficient recycling of optical phonons that will then be used to heat the carriers. In this manner, phonon up-conversion refills the optical phonon bath and directly promotes the probability of further absorbing optical phonons that in turn, amplifies the energy gain.

The optical phonon population generated by the acoustic phonon up-conversion can be introduced to our model by adding the non-equilibrium population term $p_{NE} = ap$ into the Bose-Einstein distribution p in Eq. (2a) and (2b). In this case, the total phonon occupancy can be estimated as $p_{tot} = p(\epsilon_{ph}; T) + ap(\epsilon_{ph}; T)$ (see Eq. S3 in the ESM). The non-zero constant a arises from the coupling among the acoustic modes to produce optical phonons, which strongly depends on the energies and momenta of the phonon modes involved in the processes. Hence, a demonstrates the efficiency of the acoustic-to-optical phonon up-conversion. When the acoustic phonon up-conversion fully compensates the depopulation of optical phonons, a is equal to unity. Our model predicts the non-linear increase of energy gain with increasing the phonon up-conversion efficiency a (see Fig. S8). In CsPbA₃ NCs, the value $|E|_{Max}$ can be doubled with $a = 0.5$ and can increase up to ~ 3 times with $a = 1$. A rigorous theoretical treatment accounting for all the microscopic phonon-phonon scattering processes, by including the phonon density of state and phonon dispersion of the active modes for acoustic-to-optical phonon conversion, is necessary to determine the precise value of a for each material.

In addition, semiconducting lead halide perovskites exhibit low thermal conductivity [74–76], which is an order of magnitude lower than II-VI, III-V semiconductors [77]. It implies that acoustic phonons in perovskites are more localized that enhances the probability of acoustic phonon-phonon interaction. Therefore, the recycling of lattice vibrational energy can occur more efficiently. Efficient phonon up-conversion has been recently realized in perovskite materials, which is stronger than in conventional semiconductors due to their special phonon energy spectrum [48]. The overlap between acoustic with optical branches along Γ -M and M-R paths facilitates even more the lattice energy conversion. We expect that future calculation simultaneously incorporating electron-phonon, phonon-phonon interactions and mid-gap states might be able to derive the ultimate energy gain of the phonon-assisted up-conversion process that especially can explain for the striking energy gain of $\sim 8k_B T$ in CsPbA₃ NCs.

3. Conclusion

In conclusion, we highlight the efficient up-conversion photoluminescence with striking phonon-assisted energy gain

of $\sim 8k_B T$ in high-quality all-inorganic CsPbA₃ perovskite NCs. In addition to the strong direct electron-phonon interaction, we suggest the essential contribution from acoustic phonons to the up-conversion luminescence via phonon-phonon interactions. In the non-equilibrium conditions, the acoustic phonon up-conversion recycles the population of optical modes and boosts the efficiency of photon up-conversion. The overall phonon-assisted up-conversion luminescence is a complex process, where not only light-matter but also matter-matter interactions are important. Tailor making high-quality nanomaterials and their heterostructures with strong electron-phonon interaction and low thermal conductivity such as perovskite colloidal nanocrystals may strongly promote the technologies based on up-conversion phenomenon.

4. Methods

4.1. Synthesis of CsPbA₃ nanocrystals

CsPbA₃ NCs were synthesized by following previous reports [28, 78]. The details are provided below.

4.1.1. Preparation of Cs-oleate

Cs₂CO₃ (0.407 g) was put into octadecene (ODE, 20 mL) and oleic acid (OA, 1.25 mL). This mixture was dried for 1 hour at 110°C under N₂ flowing, then heated to 150°C until Cs₂CO₃ entirely reacted with OA to form transparent solution. Since Cs-oleate precipitates out of ODE at room temperature, it has to be pre-heated to 100°C before injection.

4.1.2. Synthesis of CsPbA₃ NCs

ODE (5 mL), oleyamine (OLA, 0.5 mL), OA (0.5 mL) and PbA₂ (0.188 mmol) were put into 25 mL flask and dried under N₂ flowing for 1 hour at 110°C. After the complete dissolution of PbA₂, the temperature was raised to 160°C and the above Cs-oleate solution (0.4 mL) was quickly injected. After 5s, the reaction mixture was cooled by a water bath. For CsPbBr_xCl_{3-x}, trioctylphosphine (TOP, 0.2 mL) were added to dissolve PbA₂. The synthesized CsPbA₂ NCs were precipitated by adding 20 mL methyl acetate (MeAc), then centrifuged at 14000 RPM for 5 minutes. The depositing product was re-dispersed in 5 mL hexane and precipitated again with 5 mL MeAc and centrifuged at 14000 RPM for 5 minutes. Then the NCs were dispersed in 2mL of hexane. The solution of CsPbA₃ NCs was kept in the refrigerator at 4°C for 48 hours to precipitate excess of Cs-oleate and Pb-oleate. The NC solution was diluted and centrifuged again at 14000 RPM for 2 minutes before use.

4.2. Optical experiments

4.2.1. Linear absorption

For the NC solutions, the absorption spectra were taken by a commercial and standard set-up for UV-infrared absorption spectroscopy measurements.

4.2.2. Photoluminescence

The luminescence signals, either regular or upconverted fluorescence, were collected in a backscattering configuration. The continuous excitation sources were selected to cover the PL, one-photon and two-photon regimes for UCPL. The optical signals were collected through a microscope objective (NA = 0.45), dispersed by a single grating spectrometer and recorded by a nitrogen cooled CCD camera. The CsPbA₃ NCs were

mounted in a cryostat to allow optical excitation under vacuum conditions. To monitor the PL signal under temperature variations, the cryostat is fed by continuous flow of liquid nitrogen to control the bath temperature.

For time-resolved PL measurements, the excitation was provided by a femtosecond pulsed laser operating at 800 nm, whose frequency is doubled by a non-linear BBO crystal to provide 400 nm light. For the UCPL decay experiments, we used the 800 nm laser. All samples are investigated using the same repetition rate of 1 MHz (controlled by a pulse-picker) for all excitation photon energies. Very low excitation fluences were used in order to avoid multiexciton formation and to ensure that in each laser pulse, less than one exciton is promoted in the NC. The PL decay signal of each individual sample was filtered by suitable cut-off filters and detected by an avalanche photo diode connected to a single-phonon counter (time-correlated single photon counting).

4.2.3. Transient absorption

For transient absorption experiments, the CsPbA₃ NCs were spin-coated on sapphire substrates. The 800-nm pulse laser (repetitive rate of 1 kHz) was divided into two beams (1) to provide pump pulses at 325 nm via an optical parametric amplifier and (2) to generate broadband probe pulses after passing through a CaF₂ or sapphire crystal. Both beams were focused onto the samples by parabolic mirrors. The pump pulses excited the sample while the probe pulses, arriving after a controlled time delay, detected any pump-induced changes in the probe spectrum. The signals were recorded by a CMOS detector with spectral resolution of ~2 nm. The differential transmission $\Delta T/T$ was calculated by the relative difference between the pump-on and pump-off spectra as compared to the absolute transmission, i.e., $\Delta T/T = (T_{\text{pump-on}} - T_{\text{pump-off}})/T_{\text{pump-off}}$.

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Efficient up-conversion photoluminescence in all-inorganic lead halide perovskite nanocrystals

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Table S1. PL lifetime τ_1 , τ_2 and intensity averaged $\langle\tau\rangle$ for CsPbA₃ NCs. The corresponding decay amplitudes (C_i) are also given.

	CsPbI ₃	CsPbI _{1.5} Br _{1.5}	CsPbBr ₃	CsPbBr ₂ Cl
τ_1 (ns)	26 ± 4	24 ± 5	11 ± 2	11 ± 2
C_1	5255	2137	1988	1410
τ_2 (ns)	93 ± 10	108 ± 12	75 ± 11	90 ± 20
C_2	4356	723	367	155
$\langle\tau\rangle$ (ns)	52 ± 7	44 ± 7	21 ± 3	18 ± 4

Figure S1. UCPL versus PL spectra. (a) Comparison between normalized up-conversion (dashed lines) and regular (solid lines) PL spectra taken at $T = 296$ K for CsPbI₃ (red curves), CsPbI_{1.5}Br_{1.5} (orange curves), CsPbBr₂Cl (light-blue curves) and CsPbCl₃ (violet curves). The spectra are labelled by the corresponding halide atoms. The average quantum-yield of our synthesized NCs is about ~30%. (b) Room-temperature PL decay for CsPbI₃ NCs under excitation with photon energies of 3.10 eV (red curve) and 1.55 eV (black curve), corresponding to PL and phonon-assisted UCPL decays, respectively. Similar emission energies, linewidths, decay traces and time constants are found for PL and UCPL, indicating that the luminescence signals originate from the same exciton levels.

Figure S2. Power-dependence of PL (colored diamonds) and UCPL (colored circles, squares, triangles, stars) intensity for several excitation photon energies for (a) CsPbCl₃, (b) CsPbBr₂Cl, (c) CsPbI_{1.5}Br_{1.5} and (d) CsPbI₃ NCs. The photoexcitation energies are indicated in the plot. The colored solid lines are fittings to the experimental data by the power law $I = \alpha P^\beta$. The black dashed lines illustrate a linear power law.

Figure S3. Full PL spectrum of CsPbBr₃ NCs. The PL spectrum was taken over a wide range of energy at $T = 80$ K, showing the low-level of defects at low-energy side of the optical bandgap.

Extended discussion

S1. Exciton generation in perovskite NCs.

The average number of excitons generated in a NC ($\langle N \rangle$) by a pulse laser can be estimated by using the absorption cross section (σ) of the NC under a given pumping fluence (F): $\langle N \rangle = \sigma F$. For CsPbBr₃ NCs, $\sigma \sim 2 \times 10^{-14}$ cm² at the used excitation energy [1, 2] and the pump fluences was 35.7 μJ/cm², resulting in the estimated $\langle N \rangle \sim 1$ shown in Fig. 5 in the main text.

S2. UCPL dynamics: A three-level model

A kinetic model was previously proposed to demonstrate the phonon-assisted UCPL phenomenon [3]. In brief, the model considers an energetic diagram including a ground state $|g\rangle$, an intermediate state $|I\rangle$ defined by the excitation energy and an electronic level $|X\rangle$ (see Fig. S4) defined by the optical bandgap of the NC. The carrier is initially pumped to level $|I\rangle$ with a generation rate G , then either elastically scatters back to $|g\rangle$ (rate Γ_I) or absorbs phonon energies to level $|X\rangle$ (rate γ_{NR}). Excitons at $|X\rangle$ can non-radiatively relax to $|I\rangle$ (rate γ_{NR}) or radiative recombine (rate Γ_X).

Figure S4. Energy diagram for UCPL dynamics. A low-energy excitation (orange arrow) excites a carrier from ground state $|g\rangle$ to an intermediate state $|I\rangle$ (rate G), which can either annihilate with a rate Γ_I or transfer to the electronic level $|X\rangle$ with a rate of γ_{NR} by absorbing phonons. Excitons at $|X\rangle$ can relax to $|I\rangle$ with a rate of γ_{NR} or radiatively recombine with a rate of Γ_X . ΔE denotes the energy difference between emission and excitation energies.

In thermal equilibrium conditions, the carrier populations at $|I\rangle$ and $|X\rangle$ follow Boltzmann distribution. Hence, the transient population at each level can be described by:

$$\frac{dn_I}{dt} = G - [\Gamma_I + \gamma_{NR} \exp(-\Delta E / k_B T)] n_I + \gamma_{NR} n_X \quad (S1a)$$

$$\frac{dn_X}{dt} = \gamma_{NR} \exp(-\Delta E / k_B T) n_I - \gamma_{NR} n_X - \Gamma_X n_X \quad (S1b)$$

Solving Eq. (S1) and (S2) in equilibrium conditions (i.e., $dn_I/dt = 0$ and $dn_X/dt = 0$) results in an expression for the UCPL intensity:

$$I_{UCPL} = G \frac{c_1}{c_2 \exp(\Delta E / k_B T) + 1}, \quad (S2)$$

where $c_1 = \Gamma_X / (\Gamma_X + \gamma_{NR})$ and $c_2 = \Gamma_I / \gamma_{NR}$. We will examine the dependence of UCPL efficiency as the function of γ_{NR} , T and ΔE . The model suggests that the UCPL becomes more efficient with fast relaxation rate (see Fig. S5) and/or near resonance conditions (small ΔE) and at high temperature (see Fig. S6). Although the kinetic model can predict the influences of different factors, it cannot quantify the maximum energy gain, which can be acquired from the thermal bath of the solid. Our statistical model (see main text) is therefore proposed to solve this issue and explain for the striking energy gain of light up-conversion in perovskite nanocrystals.

Figure S5. Dependence on radiative lifetime and non-radiative relaxation. The UCPL intensity is plotted for different ratios between radiative PL lifetime and relaxation rate Γ_X/γ_{NR} . The smaller the ratio (slower radiative recombination or faster relaxation or both), the stronger the UCPL and the larger the energy gain.

Figure S6. Influence of ΔE on temperature-dependent UCPL. The UCPL intensity is plotted as a function of temperature T while using different excitation energies or in other words, different ΔE . The higher the temperature, the stronger the UCPL. Especially, for $\Delta E = 200$ meV, the temperature-dependent curve qualitatively reproduces the shape of experimental curves (see Fig. 4(b)).

S3. Statistical model

Figure S7. Influence of intermediate states on energy gain. The energy gain $|\Delta E_{\text{Max}}|$ of CsPbA₃ NCs is calculated for different values of the intermediate state lifetime $1/\gamma_{\text{NR}}$, which depends on nature of $|i\rangle$. At the ultrafast timescale (below 10^{-2} ps), $|\Delta E_{\text{Max}}|$ increases with increasing $1/\gamma_{\text{NR}}$. For the slow processes ($1/\gamma_{\text{NR}} \gg 1/\gamma_{\text{e-ph}}$), $|\Delta E_{\text{Max}}|$ saturates. In one limit, when all of $|i\rangle$ are virtual states, $1/\gamma_{\text{NR},i}$ is $\sim 1.4 \times 10^{-4}$ ps and $|\Delta E_{\text{Max}}| \sim 26$ meV as calculated in the main text. In another limit, when all of $|i\rangle$ are real states arising from, for example, defect/trap states, the lifetime $1/\gamma_{\text{NR},i}$ is in the order of 10^3 - 10^4 ps. Consequently, the energy gain increases to ~ 32 meV, which is still much smaller than the experimental value for CsPbA₃ NCs. Therefore, the nature of the intermediate states does not strongly affect the UCPL process in semiconductors.

The acoustic-acoustic annihilation is also included in our statistical model presented in the main text. In specific, Equations (2a) and (2b) can be modified as:

$$Q_{\uparrow} = \prod_{i=0}^{n-1} P_i^{\text{Abs}} = \prod_{i=0}^{n-1} (N - i) [p(\varepsilon_{\text{ph}}; T) + ap(\varepsilon_{\text{ph}}; T)] \gamma_{\text{e-ph}} \quad (\text{S3a})$$

$$Q_{\downarrow} = \prod_{i=0}^{n-1} P_i^{\text{Em}} + \prod_{i=0}^{n-1} P_i^{\text{NR}} = \prod_{i=0}^{n-1} (N + 1 - i) [p(\varepsilon_{\text{ph}}; T) + ap(\varepsilon_{\text{ph}}; T) + 1] \gamma_{\text{e-ph}} + \prod_{i=0}^{n-1} \gamma_{\text{NR},i} \quad (\text{S3b})$$

where a measures the efficiency of the acoustic-to-optical phonon up-conversion. Our model predicts a non-linear increase of the energy gain with increasing the acoustic-to-optical phonon rate.

Figure S8. UCPL energy gain enhanced by acoustic-to-optical phonon up-conversion rate. The energy gain increases with increasing a that suggests the phonon up-conversion is important to promote the UCPL ability of semiconductors.

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