


Low-threshold amplified spontaneous emission and lasing from colloidal nanocrystals of caesium lead halide perovskites

Journal Article

Author(s):

Yakunin, Sergii; Protesescu, Loredana; Krieg, Franziska; Bodnarchuk, Maryna I.; Nedelcu, Georgian; Humer, Markus; De Luca, Gabriele; [Fiebig, Manfred](#) ; Heiss, Wolfgang; Kovalenko, Maksym V.

Publication date:

2015

Permanent link:

<https://doi.org/10.3929/ethz-b-000103944>

Rights / license:

[Creative Commons Attribution 4.0 International](#)

Originally published in:

Nature Communications 6, <https://doi.org/10.1038/ncomms9056>

ARTICLE

Received 21 Apr 2015 | Accepted 13 Jul 2015 | Published 20 Aug 2015

DOI: 10.1038/ncomms9056

OPEN

Low-threshold amplified spontaneous emission and lasing from colloidal nanocrystals of caesium lead halide perovskites

Sergii Yakunin^{1,2}, Loredana Protesescu^{1,2}, Franziska Krieg^{1,2}, Maryna I. Bodnarchuk^{1,2}, Georgian Nedelcu^{1,2}, Markus Humer³, Gabriele De Luca⁴, Manfred Fiebig⁴, Wolfgang Heiss^{3,5,6} & Maksym V. Kovalenko^{1,2}

Metal halide semiconductors with perovskite crystal structures have recently emerged as highly promising optoelectronic materials. Despite the recent surge of reports on microcrystalline, thin-film and bulk single-crystalline metal halides, very little is known about the photophysics of metal halides in the form of uniform, size-tunable nanocrystals. Here we report low-threshold amplified spontaneous emission and lasing from ~ 10 nm monodisperse colloidal nanocrystals of caesium lead halide perovskites CsPbX_3 ($X = \text{Cl}, \text{Br}$ or I , or mixed Cl/Br and Br/I systems). We find that room-temperature optical amplification can be obtained in the entire visible spectral range (440–700 nm) with low pump thresholds down to $5 \pm 1 \mu\text{J cm}^{-2}$ and high values of modal net gain of at least $450 \pm 30 \text{ cm}^{-1}$. Two kinds of lasing modes are successfully observed: whispering-gallery-mode lasing using silica microspheres as high-finesse resonators, conformally coated with CsPbX_3 nanocrystals and random lasing in films of CsPbX_3 nanocrystals.

¹Department of Chemistry and Applied Biosciences, Laboratory of Inorganic Chemistry, ETH Zürich, Vladimir-Prelog-Weg 1, CH-8093 Zürich, Switzerland.

²Laboratory for Thin Films and Photovoltaics, Empa—Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland. ³Institute of Semiconductor and Solid State Physics, University Linz, Altenbergerstraße 69, 4040 Linz, Austria. ⁴Department of Materials, Laboratory for Multifunctional Ferroic Materials, ETH Zürich, Vladimir-Prelog-Weg 4, CH-8093 Zürich, Switzerland. ⁵Materials for Electronics and Energy Technology (i-MEET), Friedrich-Alexander-Universität Erlangen-Nürnberg, Martensstraße 7, 91058 Erlangen, Germany. ⁶Energie Campus Nürnberg (EnCN), Fürther Straße 250, 90429 Nürnberg, Germany. Correspondence and requests for materials should be addressed to M.V.K. (email: mvkovalenko@ethz.ch).

Recent years have seen multiple reports demonstrating outstanding optoelectronic characteristics of metal halide semiconductors with perovskite crystal structures, in the form of thin films, microcrystals and bulk single crystals^{1–11}. In particular, hybrid organic–inorganic lead halide perovskites such as MAPbX₃ (where MA = methyl ammonium and X = Cl, Br or I, or mixed Cl/Br and Br/I systems) have shown great potential as both light-absorbing and light-emitting direct-bandgap solution-deposited semiconductors. As absorber layers, MAPbX₃ materials have enabled inexpensive solar cells with certified power conversion efficiencies of up to 20% (NREL efficiency chart, www.nrel.gov)¹² and highly sensitive solution-cast photodetectors operating in the visible¹³, ultraviolet¹⁴ and X-ray¹⁵ spectra regions. Owing to their bright photoluminescence (PL), MAPbX₃ thin films and nanowires have been used in electrically driven light-emitting diodes¹⁶ and as optical gain media for lasing^{17–21}. We have recently shown that similarly high optoelectronic quality is also accessible in fully inorganic CsPbX₃ analogues, when these compounds are synthesized in the form of colloidal nanocrystals (NCs)²². In particular, CsPbX₃ NCs exhibit bright emission with PL quantum yields (QYs) reaching 90% and narrow emission linewidths of 70–100 meV (12–40 nm, for PL peaks from 410 to 700 nm, correspondingly). Precise and continuous tuning of bandgap energies over the entire visible spectral region is achievable foremost via compositional control (mixed halide Cl/Br and Br/I systems), but also through quantum-size effects. CsPbX₃ NCs appear to be largely free from mid-gap trap states, similar to their MAPbX₃ cousins²³. Both molecular solutions of MAPbX₃ and colloidal solutions of CsPbX₃ NCs share the common feature of facile solution deposition on arbitrary substrates. Further, CsPbX₃ NCs are readily miscible with other optoelectronic materials (polymers, fullerenes and other nanomaterials) and feature surface-capping ligands for further adjustments of the electronic and optical properties, and solubility in various media. We also note that CsPbX₃ NCs are formed in the pure cubic perovskite phase, in which PbX₆ octahedra are three-dimensionally interconnected by corner-sharing. In contrast, their bulk counterparts exist exclusively in wider-bandgap one-dimensional orthorhombic phases at ambient conditions^{24–26}. This disparity is most pronounced for red-emitting CsPbI₃ NCs that exhibit a narrow gap of down to 1.75 eV, whereas the corresponding bulk material has a *ca.* 1 eV larger bandgap and is yellow-colored and non-luminescent. A key practical advantage of CsPbX₃ NCs is the facile access to the blue–green spectral region of 410–530 nm via one-pot synthesis²². In comparison, common metal chalcogenide colloidal quantum dots such as CdSe NCs

need to be extremely small (≤ 5 nm) to emit in the blue–green, and as-synthesized they exhibit rather low PL QYs of $\leq 5\%$ due to mid-gap trap states. In addition, they are chemically and photochemically unstable, and require coating with an epitaxial layer of a more chemically robust, wider-gap semiconductor, such as CdS. On the other hand, narrow emission linewidths of *ca.* 100 meV, high PL QYs of up to 90% and high photochemical stability have been achieved for Cd-chalcogenide NCs as the result of two decades of research efforts to precisely engineer core-shell morphologies with independent control of the core and shell compositions and thicknesses (for example, CdSe_{core}/ZnCdS_{shell} or ‘giant-shell’ CdSe_{core}/CdS_{shell})^{27–30} and anisotropic CdSe–CdS dot-in-rod and platelet-like morphologies^{31,32}. Overall, each of these two families of colloidal semiconductors—CsPbX₃ NCs and Cd-chalcogenide nanostructures—feature their respective advantages.

Inspired by the highly efficient PL of CsPbX₃ NCs, in this study we investigate the possibility of using CsPbX₃ NCs as an inexpensive optical gain medium. First, for thin films of CsPbX₃ NCs, we report the observation of amplified spontaneous emission (ASE), tunable over most of the visible range (440–700 nm) with low pump thresholds down to $5 \pm 1 \mu\text{J cm}^{-2}$ and high values of modal net gain of at least 450 cm^{-1} . Among other colloidal semiconductor materials, such low-threshold pump fluencies have only been previously demonstrated for colloidal CdSe and CdSe/CdS nanoplatelets^{33–35}, whereas CdSe/ZnCdS NCs exhibit higher thresholds (from $800 \mu\text{J cm}^{-2}$ in the blue to $90 \mu\text{J cm}^{-2}$ in the red)²⁸ presumably due to stronger Auger recombination³⁶. We then realize two different lasing regimes for CsPbX₃ NCs depending on the resonator configuration: whispering-gallery-mode (WGM) lasing using single silica microsphere resonators, conformally coated with CsPbX₃ NCs, and random lasing in CsPbX₃ NC films.

Results

Basic characteristics of CsPbX₃ NCs in solutions and in films.

As-synthesized CsPbX₃ NCs, capped with oleylamine and oleic acid as surface ligands, form stable colloidal dispersions in typical nonpolar solvents such as toluene (Fig. 1a)²². For the spectroscopic studies in this work, we selected monodisperse samples of cubic-shaped NCs with mean sizes of *ca.* 9–10 nm (Fig. 1b). These NCs readily form uniform, compact films of sub-micron thickness on drop-casting onto a glass substrate.

The bandgap of CsPbX₃ NCs is controlled via compositional modulations, for example, by altering the Cl/Br ratio for the 410–530 nm range, and Br/I ratio for the 530–700 nm range

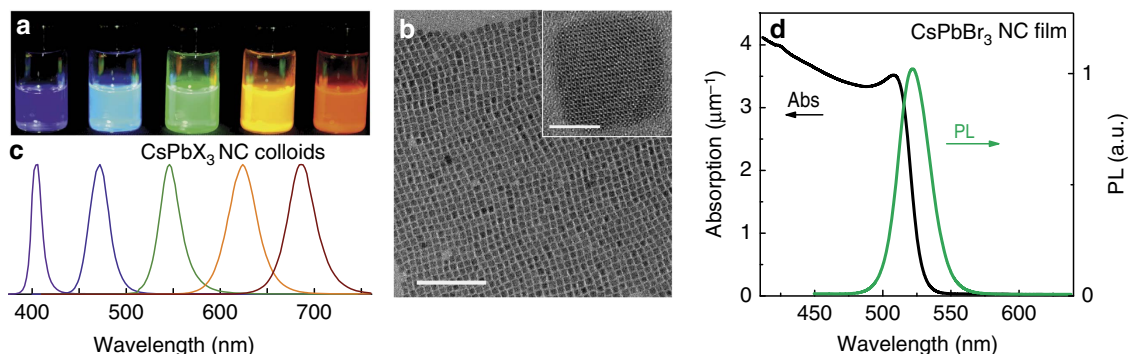


Figure 1 | Colloidal caesium lead halide perovskite NCs. (a) Stable dispersions in toluene under excitation by a ultraviolet lamp ($\lambda = 365$ nm). (b) Low- and high-resolution transmission electron microscopy images of CsPbBr₃ NCs; corresponding scale bars are 100 and 5 nm. (c) PL spectra of the solutions shown in (a). (d) Optical absorption and PL spectra of a *ca.* 400-nm-CsPbBr₃ NC film.

(Fig. 1c). A pronounced excitonic peak is preserved in the absorption spectrum of the CsPbBr₃ NC film (Fig. 1d). The absorption coefficients of the densely packed films are in the range of $(3.6\text{--}4.0) \cdot 10^4 \text{ cm}^{-1}$ (or $3.6\text{--}4.0 \mu\text{m}^{-1}$), indicating that up to 70–80% of the pumping laser light ($\lambda = 400 \text{ nm}$) is absorbed by 300–400-nm thick films. The refractive index of a CsPbBr₃ NC film is estimated to be 1.85–2.30 at 400–530 nm from the optical reflectance and absorption spectra (Supplementary Fig. 1). The PL from this NC film exhibits a peak with a narrow linewidth of 25 nm (110 meV), Stokes-shifted by 13 nm (57 meV) with respect to the excitonic absorption peak (Fig. 1d). The PL QYs of the same NCs in the solution reach values of up to 70–90% (for green-to-red-emitting NCs) indicating a high degree of electronic surface passivation. The PL lifetimes are very similar for solutions and for films (Supplementary Fig. 2; 1–22 ns, longer for lower-bandgap NCs). PL excitation spectrum from an NC film closely resembles the absorption spectrum (Supplementary Fig. 3).

Amplified spontaneous emission from CsPbX₃ NCs. Clear signatures of the ASE emission—narrowing of the emission peaks and threshold behaviour with a steep rise in intensity above the threshold—are readily obtained from 300- to 400-nm thick films produced by drop-casting colloidal solutions onto glass substrates (Fig. 2a; excitation at 400 nm with 100 fs pulses; and Supplementary Fig. 4 presenting ASE/PL on a logarithmic scale in

a wider range of pumping intensities). ASE is spectrally different from PL emission; it has a narrower bandwidth of 4–9 nm (full width at half maximum, FWHM; see Supplementary Fig. 5) due to a narrow gain in bandwidth and is red-shifted by *ca.* 10 nm with respect to the PL maximum. When the ASE spectrum is overlaid with the Tauc plot of the direct-bandgap absorption (Supplementary Fig. 3), the ASE spectral maxima coincide with the end of the shallow absorption tail (Urbach tail). This red-shifted ASE may have its origins in re-absorbance during single-exciton lasing^{28,29} or in the excitonic binding energies in the bi-excitonic optical gain mechanism^{34,37}. Similar to PL spectra, ASE can be obtained in the whole visible spectral region by varying the composition of CsPbX₃ NCs (Fig. 2b). The threshold for building ASE is *ca.* $5 \pm 1 \mu\text{J cm}^{-2}$ (Fig. 2c) for CsPbBr₃ perovskite NCs, and generally falls in the range of 5–22 $\mu\text{J cm}^{-2}$ for all other compositions (Supplementary Fig. 6). Notably, the ASE linewidth increases for samples with a lower ASE threshold suggesting that a larger portion of the emission falls within the optical gain conditions, enlarging the optical gain bandwidth.

In addition to the ASE threshold, the net modal gain is an important figure-of-merit that, from a practical point of view, indicates the efficiency of light amplification in the material and the quality of the resonator needed for achieving lasing³⁸. Optical gain can be measured by using the variable stripe length method³⁹, where the excitation light is shaped into a line of variable lengths on the sample surface (see the schematics in the inset of Fig. 2d and a photograph of the emitted light in

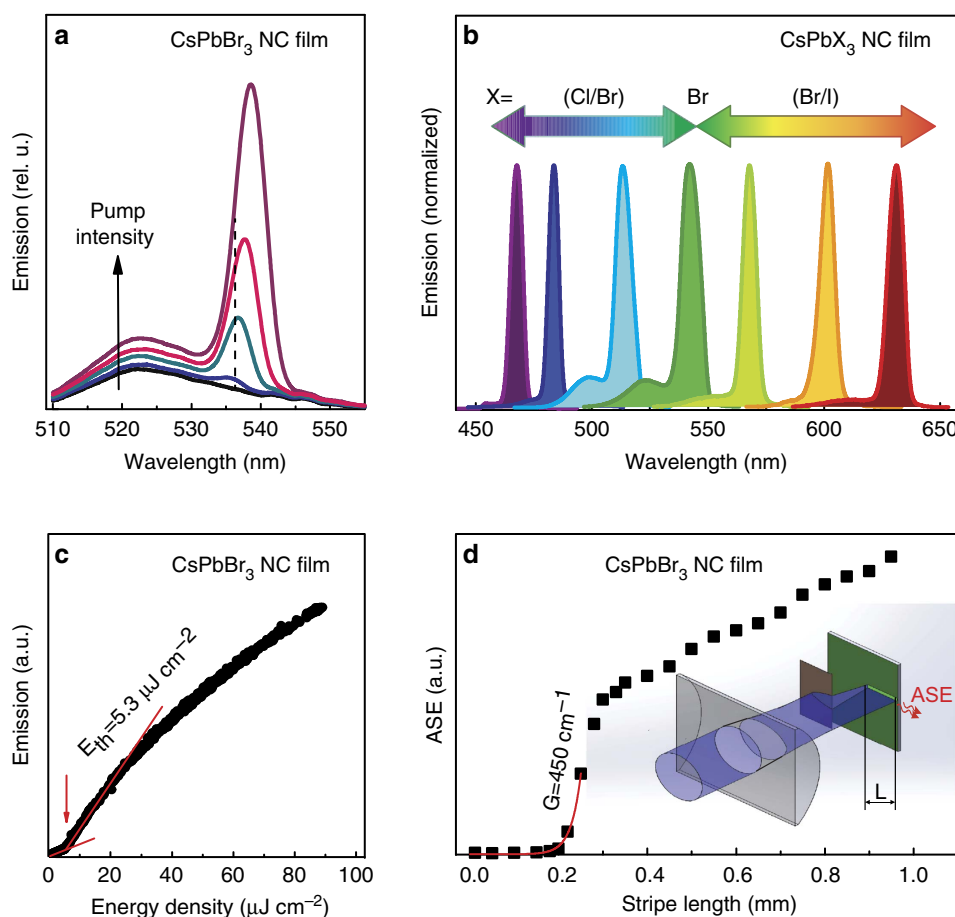


Figure 2 | ASE spectra from thin films of CsPbX₃ NCs. (a) Pump-fluence dependence of the emission from a CsPbBr₃ NC film (pumping intensity range was 3–25 $\mu\text{J cm}^{-2}$). (b) Spectral tunability of ASE via compositional modulation. (c) Threshold behaviour for the intensity of the ASE band of the CsPbBr₃ NC film shown in (a). (d) Variable stripe-length experiment for estimation of modal net gain for the CsPbBr₃ NC film. All spectra were excited at $\lambda = 400 \text{ nm}$ with 100 fs laser pulses.

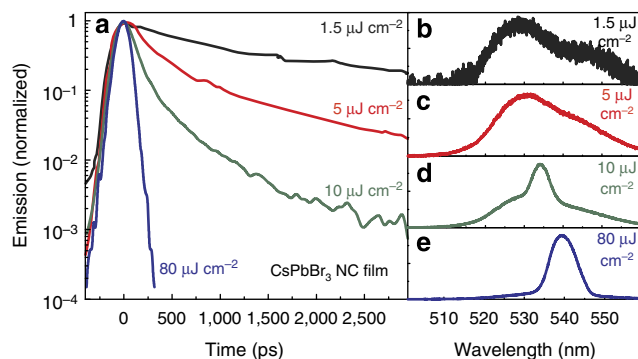


Figure 3 | Time-resolved measurements from the CsPbBr₃ NC film. (a) Decay traces at pump fluences varied from subthreshold to well above ASE threshold values with emission recorded at ASE peak wavelengths. (b–e) The corresponding full emission spectra.

Supplementary Fig. 7), and the emission intensity is then measured as a function of stripe length, L . When the stripe length reaches the threshold value where propagation losses are compensated by the optical amplification, the PL spectrum starts to show an additional ASE component that grows with stripe length (see Fig. 2d and corresponding spectra in Supplementary Fig. 8). The threshold region can be fitted with the model of net modal gain (G): $I = \frac{A}{g}(e^{GL} - 1)$, yielding high values of G ranging from 450 to 500 cm^{-1} . Considering these gain values, the build-up time for ASE was estimated to be 140 fs, considerably shorter than the ASE threshold lifetime of 300 ps.

Another characteristic and expected feature of ASE, seen in time-resolved experiments (Fig. 3), is the acceleration of radiative recombination due to switch from individual to collective emission. For CsPbBr₃ NC films in this work, at excitation intensities lower than the ASE threshold ($< 2 \mu\text{J cm}^{-2}$; Fig. 3b), typical PL lifetimes of several nanoseconds are observed with nearly single-exponent behaviour. Well above ASE thresholds ($80 \mu\text{J cm}^{-2}$; Fig. 3e), ASE lifetimes of 60 ps were estimated, again with clean, single-exponent line shape. At the ASE threshold, an ASE lifetime of 300 ps can be roughly estimated from a bi-exponential fit assuming competing ASE and PL processes. A ‘quasi-continuous wave’ regime of excitation can be observed with pumping pulses of longer duration than this ASE lifetime²⁷, though at the expense of higher overall pumping fluence to maintain the same instant excitation intensity over the whole pulse duration. Such pulses can be provided by conventional, inexpensive nanosecond lasers. In this case, with a 300-ps ASE lifetime at 5–10 $\mu\text{J cm}^{-2}$ femtosecond pumping thresholds, we estimate a threshold fluence of 150–300 $\mu\text{J cm}^{-2}$ for 10-ns excitation pulses. In close agreement, ASE thresholds of 400–500 $\mu\text{J cm}^{-2}$ were observed experimentally (Fig. 4).

Whispering-gallery-mode lasing from CsPbX₃ NCs. Effective optical feedback from a high-quality optical resonator is needed to obtain lasing. In this regard, commercially available silica microspheres can serve as circular cavities in which the emitted light orbits around the circumference due to total internal reflection (Fig. 5a, inset). The resulting cavity modes are known as WGMs. WGM lasers can be conveniently observed by the adhesion of solution-processed lasing material onto the surface of the microspheres^{17,40,41}. The great utility of microsphere resonators for research purposes stems from their extremely high and wavelength-independent Q factors of up to 10^9 (describing the degree of feedback of the cavity), and their rather isotropic leakage of the emitted light. In this work, we obtained well-resolved lasing

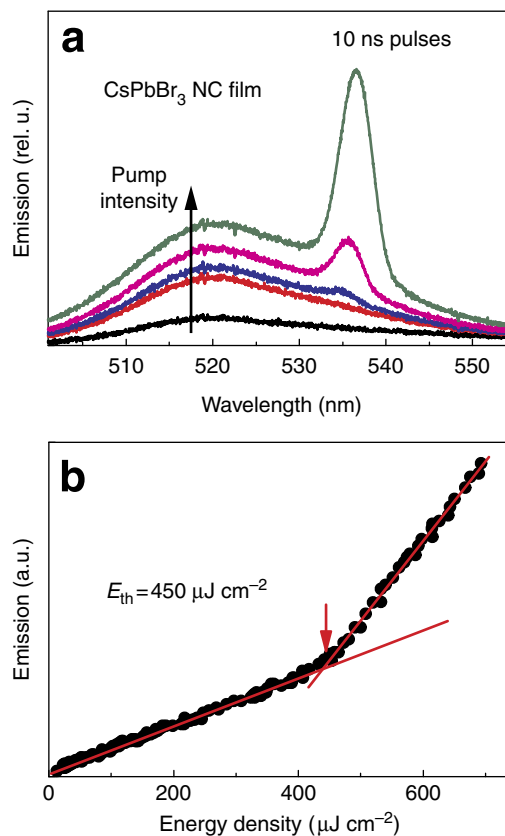


Figure 4 | ASE from CsPbBr₃ NC film under nanosecond excitation.

(a) Evolution of the emission spectra with the increase of pumping fluence and (b) corresponding dependence of the emission at 535 nm on pump fluence. Spectra were excited at $\lambda = 355 \text{ nm}$ with 10 ns laser pulses.

modes with pumping threshold behaviour using 15 μm (Fig. 5a) and 53 μm (Supplementary Fig. 9) spheres, with intermodal distances dependent on the sphere diameter (the larger the sphere, the smaller the spacing). All spectra were excited at the wavelength 400 nm with 100 fs laser pulses. The observed linewidths of lasing modes (0.15–0.20 nm) are limited primarily by the resolution of the spectrometer used for detection. We note that the spectra presented herein were collected from single microspheres using a microscope objective. In contrast, when the emission from several spheres was integrated, lasing modes were often indistinguishable due to the small but essential standard size-deviation of the spheres of *ca.* 0.5–1%.

Random lasing from CsPbX₃ nanocrystals. Lasing can also be observed without optical resonators, namely when the required optical feedback is provided via light scattering induced by intrinsic disorder in the lasing medium, leading to so-called random lasing⁴². Light diffuses in highly scattering media and randomly forms closed loops causing random fluctuations of lasing modes. Scattering occurs, for instance, on the aggregates of NCs, and is clearly pronounced in thicker films of several microns, since the path of the light is unique and irreproducible, so are the lasing modes (Fig. 5b) generated by each shot of the pumping laser. For the CsPbX₃ NC films investigated in this work, the modes appear to be fully stochastic and their distribution for 256 consecutive laser shots is presented in Fig. 5c.

The multiple emission spectra expressed as a function of wave vector in k space, shown in Fig. 5c, can be Fourier transformed into

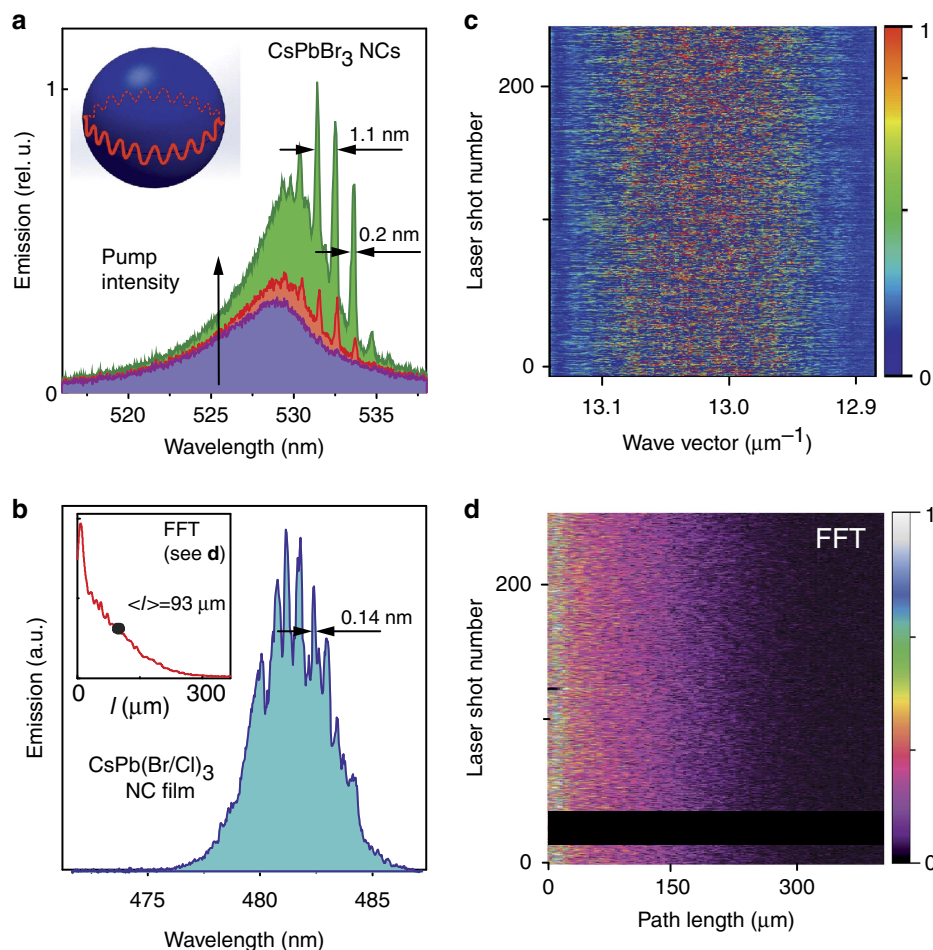


Figure 5 | Lasing in perovskite CsPbX₃ NC films. (a) Evolution from PL to whispering-gallery-mode (WGM) lasing with increasing pump intensity in a microsphere resonator of 15 μm in diameter, covered by a film of CsPbBr₃ NCs. (b) Single pump laser shot mode structure of random lasing from CsPb(Br/Cl)₃ NC film. The inset shows path-length distribution averaged over 256 pump laser shots. (c) Stochastic mode distribution in a series of 256 pump laser shots (PL background emission is subtracted). (d) Fast Fourier transform (FFT) of (c).

a corresponding optical path-length distribution (Fig. 5d). The averaged distribution of path length, l , over 256 shots is presented in the inset of Fig. 5b. The mean path length, $\langle l \rangle = 93 \pm 5 \mu\text{m}$, is obtained by integral averaging over the path-length range of 0–300 μm. The criterion for Anderson localization, $k \langle l \rangle \approx 10^3$, is much larger than unity, pointing to the case of weakly scattering random lasing. The medium is rather transparent and shows no apparent effects from film imperfections such as cracks and pinholes. The lasing threshold is of the same order of magnitude as ASE threshold discussed above. Due to the strong increase in intensity of Rayleigh scattering with decreasing wavelength ($I \propto \lambda^{-4}$), aggregation-induced scattering and hence random lasing is most pronounced in blue-emitting samples, such as the one shown in Fig. 5b.

Discussion

Considering the colloidal nature of CsPbX₃ NCs, the most relevant comparison to be drawn is with strongly quantum-confined Cd-chalcogenide-based colloidal NCs. After the first demonstration of optical gain and stimulated emission from colloidal CdSe NCs (emission at 620 nm) in 2000 (ref. 37), colloidal NCs have been considered as an eventual alternative to more expensive epitaxial group III–V materials (for example,

InGaN, GaAsP and InGaAs). The green spectral region is especially difficult to access by III–V compounds⁴³. For this reason, the size-tunable emission of Cd-chalcogenide-based materials is highly appealing, but still lacks stability in the blue spectral region ($\leq 500 \text{ nm}$)²⁹. So far, the lowest pumping thresholds of Cd-based quantum dots (QDs) have been reported for specially engineered CdSe/ZnCdS core-shell structures, ranging from $90 \mu\text{J cm}^{-2}$ for red QDs to $800 \mu\text{J cm}^{-2}$ for blue QDs with single-exciton nature of the optical gain²⁸. Recently, a large step forward was made by introducing pristine CdSe and core-shell CdSe/CdS nanoplatelets^{35,44,45}, showing the lowest ASE thresholds for inorganic colloidal nanomaterials obtained to date ($6 \mu\text{J cm}^{-2}$ at 520 nm and $8 \mu\text{J cm}^{-2}$ at 635 nm)^{34,35}. Furthermore, in such atomically flat CdSe nanoplatelets, where bandgaps are tunable stepwise by adjusting the number of unit cells in platelet thickness, only discrete emission wavelengths were so far demonstrated and ASE had not been reported below 510 nm. Overall, in Cd-chalcogenide-based systems, emission wavelength tuning is almost exclusively achieved via quantum-size effects. On the contrary, in this study rather large CsPbX₃ NCs (9–10 nm) with weak to no quantum confinement were chosen and the emission was found to be freely adjustable via compositional tuning (that is, by the halide ratio). Such convenient

compositional tuning is not easily accessible in Cd-chalcogenide NCs. In experiments on smaller CsPbBr₃ NCs with pronounced quantum-size effects, by up to an order of magnitude higher ASE thresholds were observed. Thus, a clear complementarity is seen between weakly confined CsPbX₃ NCs (performing best in the blue–green with $\leq 10 \mu\text{J cm}^{-2}$ blue ASE thresholds) and strongly confined Cd-chalcogenide-based materials (performing best in the green–red with $\leq 10 \mu\text{J cm}^{-2}$ ASE thresholds for red CdSe/CdS platelets). For a completely unbiased comparison, we have reproduced the synthesis of CdSe and core-shell CdSe/CdS nanoplatelets described by She *et al.*³⁵, and observed same low thresholds of $7\text{--}15 \mu\text{J cm}^{-2}$ (Supplementary Figs 10 and 11) under the same testing conditions as applied here for CsPbX₃ NCs using femtosecond excitations. For nanosecond excitation pulses (Fig. 4), ASE thresholds for CsPbX₃ NCs rise to $\sim 0.45 \text{ mJ cm}^{-2}$ (and 1 mJ cm^{-2} for CdSe/CdS nanoplatelets; see Supplementary Fig. 12). Low ASE thresholds in CsPbX₃ NCs are also assisted by an extremely large absorption cross-section (σ). For CsPbBr₃ perovskite NCs, we estimated $\sigma = 8 \times 10^{-14} \text{ cm}^2$ (or 8 nm^2), that is almost two orders of magnitude larger than typically reported for CdSe QDs⁴⁶, and similar to CdSe nanoplatelets⁴⁷, emitting in the same wavelength range (green). No continuous-wave ASE could be observed at room temperature or down to 80 K for neither CsPbX₃ NCs nor for Cd-chalcogenide platelets, up to excitation levels causing photo-damage of the samples.

A comparison of our results for CsPbX₃ NCs with reports on closely related solution-deposited hybrid perovskite MAPbX₃ films and microcrystals points to rather similar ASE thresholds (Supplementary Table 1)^{17–20}. MAPbX₃ films were also reported to exhibit random lasing⁴⁸, lasing from vertical cavities²⁰ and from spherical resonators¹⁷ and WGM lasing¹⁹. The comparably good performance of CsPbBr₃ NCs indicates that their high surface area does not impede their optical properties. Also the solution-processed organic semiconductor materials exhibit similar ASE thresholds under similar testing conditions (no cavity, plane wave-guiding films)⁴⁹. So far, in only a few examples of vacuum-deposited organic semiconductors⁵⁰ and epitaxial multiple-quantum-well structures⁵¹ were lower, sub- $\mu\text{J cm}^{-2}$ ASE thresholds demonstrated, but usually with an order of magnitude lower optical gain values. At the time of the submission of this work, much lower thresholds ($0.22 \mu\text{J cm}^{-2}$) were reported by Zhu *et al.*²¹, for lasing from MAPbI₃ wires, highlighting also the morphological effects (wire acts as a single-mode waveguide and laser resonator) and suggesting that future studies should focus on engineering CsPbX₃ wire-like morphologies with dimensions comparable to the wavelengths of light. As a first step in this direction and due to the lack of reports on bulk-like CsPbX₃, we have prepared CsPbX₃ polycrystalline films (with crystalline domain sizes of several μm) and individual microcrystals simply by drop-casting from dimethylformamide solutions and inspected their PL/ASE characteristics. NCs and microcrystals of the same composition exhibit nearly identical PL peak wavelengths and linewidths, and radiative lifetimes (Supplementary Fig. 13). ASE thresholds of polycrystalline films were by an order of magnitude higher, but this may well be caused also by the difficult-to-control, suboptimal for ASE build-up morphologies of these films. Similarly to CsPbX₃ NCs, the ASE peaks were found to be red-shifted with respect to the PL maxima (Supplementary Fig. 14). For selected large microcrystals (100–150 μm) clear WGM lasing modes were observed as well (Supplementary Fig. 15). No wire-like morphologies could be found for direct comparison with MAPbI₃ wires. Overall, we conclude that among the three distinct cases—small CsPbX₃ QDs (4–8 nm, chemically unstable), CsPbX₃ NCs (10 nm) and CsPbX₃ microcrystals—the NCs exhibit the best balance between

optical performance (having generally the lowest ASE thresholds) and chemical versatility (exhibiting facile solution processing, and easily adjustable film thickness and morphology for obtaining various lasing regimes).

At present, we cannot fully answer the remaining question of this study—the exact mechanism for optical gain. This is also an open question in the MAPbX₃-related literature. To speculate on this matter for CsPbX₃ NCs, the observed red shift of the ASE peaks with respect to PL maxima can be explained by either bi-excitonic lasing (due to binding energy of bi-exciton)³⁷ or by self-absorption in the case of a single-exciton gain^{28,29}. We also evaluated the average density of excitons per each NC ($\langle N \rangle$, for details, see Supplementary Note 1) at the ASE threshold and found $\langle N \rangle = 0.5 \pm 0.15$. Expected theoretical values of $\langle N \rangle$ are 0.5 for single-exciton gain²⁹ and 1 for bi-excitonic mechanism^{37,52}. Increase of QY with pump intensity (Supplementary Fig. 16) might be another plausible evidence for single-exciton gain, as QY should decrease when Auger recombination is limiting the ASE (typically observed for bi-excitonic gain).

In summary, perovskite CsPbX₃ NCs, synthesized via a simple one-step reaction between PbX₂ and Cs-oleate in nonpolar solvent media, are particularly promising for achieving ASE/lasing in blue and green spectral regions. Optical gain is demonstrated here at room temperature for pulse durations of up to 10 ns, corresponding to the quasi-continuous wave (quasi-cw) excitation regime with low ASE threshold values down to $5 \mu\text{J cm}^{-2}$. High optical gain values of up to 450 cm^{-1} allow for obtaining resonant conditions for lasing either by coating CsPbX₃ NCs onto spherical microresonators or via random lasing mediated by light scattering on NC aggregates. Random lasing, arising from the combined effect of wave guiding and light scattering in the optical gain medium of densely packed aggregates of CsPbX₃ NCs, does not require an ultraprecise cavity as in conventional lasing. This not only provides the obvious technological advantage of facile and inexpensive fabrication, but also enables various niche applications such as displays and lighting, benefitting from the broad spectral angular distribution of the random lasing^{42,53}. Another promising area of application for random lasers, benefitting from the broad ASE spectrum, is as the light source in optical coherence tomography where it is critical to keep optical coherence moderately low but controlled^{54,55}. Random lasing in the weak-scattering regime, where the spectral distribution of lasing modes is unique for each laser shot, can serve as a physically based method for random number generation and in cryptography⁵⁶.

Methods

Preparation of CsPbX₃ NCs and microcrystalline films. CsPbX₃ NCs were synthesized as described in our recent report²². The crude solution was cooled down with water bath and aggregated NCs were separated by centrifuging for 3 min at 11,000 r.p.m. After centrifugation, the supernatant was discarded, the particles were redispersed in 0.3 ml hexane and centrifuged again for 4 min at 12,000 r.p.m. After repeating the previous step one more time, the precipitate was redispersed in 0.6 ml toluene, and 0.2 ml acetonitrile was added for precipitation. The NCs were centrifuged again for 4 min at 12,000 r.p.m., and after this, the supernatant was discarded and the precipitate was redispersed in toluene. Thin films of CsPbX₃ NCs were obtained by drop-casting 10–50 μl of CsPbX₃ NC solution at ambient conditions onto glass substrates, followed by drying at ambient conditions. For coating CsPbX₃ NCs onto silica microspheres, water-dispersed 15- and 53- μm silica microspheres (<http://www.microspheres-nanospheres.com>) were first drop-cast onto a hot glass substrate, followed by drop-casting of CsPbX₃ NCs. For preparing microcrystalline films, PbX₂ and CsX were dissolved in dimethylformamide, and then drop- or spin-cast onto a glass substrate followed by heat treatment at 150 °C. Alternatively, films of PbX₂ can be converted into CsPbX₃ on dipping into Cs-halide solutions.

Characterization of CsPbX₃ NC solutions and films. UV-Vis absorption and reflection spectra of the NC films were collected using a Jasco V670 spectrometer

equipped with an integrating sphere. Steady-state PL emission and excitation spectra were acquired with a Fluorolog iHR320 Horiba Jobin Yvon spectrofluorometer, equipped with Xe lamp and a photomultiplier tube (PMT) detector. PL lifetime measurements were performed using a time-correlated single-photon counting setup, equipped with SPC-130-EM counting module (Becker & Hickl GmbH) and an IDQ-ID-100-20-ULN avalanche photodiode (Quantique) for recording the decay traces. The emission of the perovskite NCs was excited by a 400-nm 100-fs laser pulses with a repetition of 1 kHz synchronized to time-correlated single-photon counting module through an electronic delay generator (DG535 from Stanford Research Systems). Transmission electron microscopy images were recorded using a JEOL JEM-2200FS microscope operated at 200 kV. For the thickness determination of the films, an AlphaStep D-120 profilometer was used.

ASE and lasing experiments. These experiments were performed with excitation light from nanosecond and femtosecond lasers. All experiments were conducted at room temperature. The femtosecond laser system consisted of an oscillator (Vitesse 800) and an amplifier (Legend Elite), both from Coherent Inc., with a frequency-doubling external beta barium borate (BBO) crystal; it yielded 100 fs pulses at 400 nm, with a repetition rate of 1 kHz and pulse energy of up to 4 μ J. The laser beam profile had a TEM₀₀ mode with a 1-mm FWHM diameter. Laser power was measured by a LabMax-TOP laser energy meter (Coherent Inc.) with a nJ-measuring head. For variable stripe length (VSL) experiments, the beam was focused into a stripe by a cylindrical lens with a focal length of 75 mm. The nanosecond laser system was a Quanta-Ray Pro 230-50 (Spectra-Physics), frequency tripled to 355 nm, with a pulse duration of 10 ns and a top-hat beam profile focused to a spot of 1.5 mm in diameter with a pulse energy of up to 30 μ J. To resolve the spectrally sharp lasing peaks, the optical emission was coupled into a Princeton Instruments SP-2300i spectrometer, equipped with a Thorlabs LC100/M CCD detector array (0.14 nm resolution). Fast Fourier Transform (FFT) analysis of random lasing mode patterns for large arrays of pump laser shots was performed using the Gwyddion software package. The laser beam intensity profiles were analysed by a LabMax-TOP camera from Coherent Inc.

References

- Gratzel, M. The light and shade of perovskite solar cells. *Nat. Mater.* **13**, 838–842 (2014).
- Green, M. A., Ho-Baillie, A. & Snaith, H. J. The emergence of perovskite solar cells. *Nat. Photon.* **8**, 506–514 (2014).
- Park, N. G. Organometal perovskite light absorbers toward a 20% efficiency low-cost solid-state mesoscopic solar cell. *J. Phys. Chem. Lett.* **4**, 2423–2429 (2013).
- Zhou, H. *et al.* Interface engineering of highly efficient perovskite solar cells. *Science* **345**, 542–546 (2014).
- Chung, I., Lee, B., He, J., Chang, R. P. & Kanatzidis, M. G. All-solid-state dye-sensitized solar cells with high efficiency. *Nature* **485**, 486–489 (2012).
- Stranks, S. D. *et al.* Electron-hole diffusion lengths exceeding 1 micrometer in an organometal trihalide perovskite absorber. *Science* **342**, 341–344 (2013).
- Xing, G. *et al.* Long-range balanced electron- and hole-transport lengths in organic-inorganic CH₃NH₃PbI₃. *Science* **342**, 344–347 (2013).
- Nie, W. *et al.* High-efficiency solution-processed perovskite solar cells with millimeter-scale grains. *Science* **347**, 522–525 (2015).
- Dong, Q. *et al.* Electron-hole diffusion lengths > 175 μ m in solution-grown CH₃NH₃PbI₃ single crystals. *Science* **347**, 967–970 (2015).
- Shi, D. *et al.* Low trap-state density and long carrier diffusion in organolead trihalide perovskite single crystals. *Science* **347**, 519–522 (2015).
- Zhang, F. *et al.* Brightly luminescent and color-tunable colloidal CH₃NH₃PbX₃ (X = Br, I, Cl) quantum dots: potential alternatives for display technology. *ACS Nano* **9**, 4533–4542 (2015).
- Jeon, N. J. *et al.* Compositional engineering of perovskite materials for high-performance solar cells. *Nature* **517**, 476–480 (2015).
- Dou, L. *et al.* Solution-processed hybrid perovskite photodetectors with high detectivity. *Nat. Commun.* **5**, 5404 (2014).
- Guo, Y. L., Liu, C., Tanaka, H. & Nakamura, E. Air-stable and solution-processable perovskite photodetectors for solar-blind UV and visible light. *J. Phys. Chem. Lett.* **6**, 535–539 (2015).
- Yakunin, S. *et al.* Detection of X-ray photons by solution-processed lead halide perovskites. *Nat. Photon.* **9**, 444–449 (2015).
- Tan, Z. K. *et al.* Bright light-emitting diodes based on organometal halide perovskite. *Nat. Nanotechnol.* **9**, 687–692 (2014).
- Sutherland, B. R., Hoogland, S., Adachi, M. M., Wong, C. T. & Sargent, E. H. Conformal organohalide perovskites enable lasing on spherical resonators. *ACS Nano* **8**, 10947–10952 (2014).
- Xing, G. *et al.* Low-temperature solution-processed wavelength-tunable perovskites for lasing. *Nat. Mater.* **13**, 476–480 (2014).
- Zhang, Q., Ha, S. T., Liu, X., Sum, T. C. & Xiong, Q. Room-temperature near-infrared high-Q perovskite whispering-gallery planar nanolasers. *Nano Lett.* **14**, 5995–6001 (2014).
- Deschler, F. *et al.* High photoluminescence efficiency and optically pumped lasing in solution-processed mixed halide perovskite semiconductors. *J. Phys. Chem. Lett.* **5**, 1421–1426 (2014).
- Zhu, H. *et al.* Lead halide perovskite nanowire lasers with low lasing thresholds and high quality factors. *Nat. Mater.* **14**, 636–642 (2015).
- Protesescu, L. *et al.* Nanocrystals of cesium lead halide perovskites (CsPbX₃, X = Cl, Br, and I): novel optoelectronic materials showing bright emission with wide color gamut. *Nano Lett.* **15**, 3692–3696 (2015).
- Oga, H., Saeki, A., Ogomi, Y., Hayase, S. & Seki, S. Improved understanding of the electronic and energetic landscapes of perovskite solar cells: high local charge carrier mobility, reduced recombination, and extremely shallow traps. *J. Am. Chem. Soc.* **136**, 13818–13825 (2014).
- Sharma, S., Weiden, N. & Weiss, A. Phase diagrams of quasibinary systems of the type: ABX₃-A'BX₃; ABX₃-AB'X₃ and ABX₃-ABX'₃; X = halogen. *Z. Phys. Chem.* **175**, 63–80 (1992).
- Trots, D. M. & Myagkota, S. V. High-temperature structural evolution of caesium and rubidium triiodoplumbates. *J. Phys. Chem. Solids* **69**, 2520–2526 (2008).
- Stoumpos, C. C., Malliakas, C. D. & Kanatzidis, M. G. Semiconducting tin and lead iodide perovskites with organic cations: phase transitions, high mobilities, and near-infrared photoluminescent properties. *Inorg. Chem.* **52**, 9019–9038 (2013).
- Wang, Y. *et al.* Blue liquid lasers from solution of CdZnS/ZnS ternary alloy quantum dots with quasi-continuous pumping. *Adv. Mater.* **27**, 169–175 (2015).
- Dang, C. *et al.* Red, green and blue lasing enabled by single-exciton gain in colloidal quantum dot films. *Nat. Nanotechnol.* **7**, 335–339 (2012).
- Dang, C. & Nurmikko, A. Beyond quantum dot LEDs: optical gain and laser action in red, green, and blue colors. *MRS Bull.* **38**, 737–742 (2013).
- Chen, O. *et al.* Compact high-quality CdSe–CdS core-shell nanocrystals with narrow emission linewidths and suppressed blinking. *Nat. Mater.* **12**, 445–451 (2013).
- Carbone, L. *et al.* Synthesis and micrometer-scale assembly of colloidal CdSe/CdS nanorods prepared by a seeded growth approach. *Nano Lett.* **7**, 2942–2950 (2007).
- Mahler, B., Nadal, B., Bouet, C., Patriarche, G. & Dubertret, B. Core/shell colloidal semiconductor nanoplatelets. *J. Am. Chem. Soc.* **134**, 18591–18598 (2012).
- Lhuillier, E. *et al.* Two-dimensional colloidal metal chalcogenides semiconductors: synthesis, spectroscopy, and applications. *Acc. Chem. Res.* **48**, 22–30 (2015).
- Grim, J. Q. *et al.* Continuous-wave biexciton lasing at room temperature using solution-processed quantum wells. *Nat. Nanotechnol.* **9**, 891–895 (2014).
- She, C. *et al.* Low-threshold stimulated emission using colloidal quantum wells. *Nano Lett.* **14**, 2772–2777 (2014).
- Robel, I., Gresback, R., Kortshagen, U., Schaller, R. D. & Klimov, V. I. Universal size-dependent trend in Auger recombination in direct-gap and indirect-gap semiconductor nanocrystals. *Phys. Rev. Lett.* **102**, 177404 (2009).
- Klimov, V. I. *et al.* Optical gain and stimulated emission in nanocrystal quantum dots. *Science* **290**, 314–317 (2000).
- Coldren, L. A., Corzine, S. W. & Mašanović, M. L. in *Diode Lasers and Photonic Integrated Circuits* 247–333 (John Wiley & Sons, Inc., 2012).
- Shaklee, K. L. & Leheny, R. F. Direct determination of optical gain in semiconductor crystals. *Appl. Phys. Lett.* **18**, 475–477 (1971).
- Grivas, C. *et al.* Single-mode tunable laser emission in the single-exciton regime from colloidal nanocrystals. *Nat. Commun.* **4**, 2376 (2013).
- Xing, G. *et al.* Ultralow-threshold two-photon pumped amplified spontaneous emission and lasing from seeded CdSe/CdS nanorod heterostructures. *ACS Nano* **6**, 10835–10844 (2012).
- Wiersma, D. S. The physics and applications of random lasers. *Nat. Phys.* **4**, 359–367 (2008).
- Laubsch, A., Sabathil, M., Baur, J., Peter, M. & Hahn, B. High-power and high-efficiency InGaN-based light emitters. *IEEE Trans. Electron Devices* **57**, 79–87 (2010).
- Ithurria, S. *et al.* Colloidal nanoplatelets with two-dimensional electronic structure. *Nat. Mater.* **10**, 936–941 (2011).
- Tessier, M. D. *et al.* Efficient exciton concentrators built from colloidal core/crown CdSe/CdS semiconductor nanoplatelets. *Nano Lett.* **14**, 207–213 (2014).
- Leatherdale, C. A., Woo, W. K., Mikulec, F. V. & Bawendi, M. G. On the absorption cross section of CdSe nanocrystal quantum dots. *J. Phys. Chem. B* **106**, 7619–7622 (2002).
- Kunneman, L. T. *et al.* Nature and decay pathways of photoexcited states in CdSe and CdSe/CdS nanoplatelets. *Nano Lett.* **14**, 7039–7045 (2014).
- Dhanker, R. *et al.* Random lasing in organo-lead halide perovskite microcrystal networks. *Appl. Phys. Lett.* **105**, 151112 (2014).
- Namdas, E. B. *et al.* Low thresholds in polymer lasers on conductive substrates by distributed feedback nanoimprinting: progress toward electrically pumped plastic lasers. *Adv. Mater.* **21**, 799–802 (2009).

50. Kozlov, V. G., Bulovic, V., Burrows, P. E. & Forrest, S. R. Laser action in organic semiconductor waveguide and double-heterostructure devices. *Nature* **389**, 362–364 (1997).
51. Thijs, P. J. A., Tiemeijer, L. F., Kuindersma, P. I., Binsma, J. J. M. & Van Dongen, T. High-performance 1.5 μm wavelength InGaAs-InGaAsP strained quantum well lasers and amplifiers. *IEEE J. Sel. Top. Quantum Electron.* **27**, 1426–1439 (1991).
52. Klimov, V. I. *et al.* Single-exciton optical gain in semiconductor nanocrystals. *Nature* **447**, 441–446 (2007).
53. Cao, H. Lasing in random media. *Waves Random Media* **13**, R1–R39 (2003).
54. Redding, B., Choma, M. A. & Cao, H. Speckle-free laser imaging using random laser illumination. *Nat. Photon.* **6**, 355–359 (2012).
55. Redding, B. *et al.* Low spatial coherence electrically pumped semiconductor laser for speckle-free full-field imaging. *Proc. Natl Acad. Sci. USA* **112**, 1304–1309 (2015).
56. Reidler, I., Aviad, Y., Rosenbluh, M. & Kanter, I. Ultrahigh-speed random number generation based on a chaotic semiconductor laser. *Phys. Rev. Lett.* **103**, 024102 (2009).

Acknowledgements

M.V.K. acknowledges financial support from the European Union through the FP7 (ERC Starting Grant NANOSOLID, GA No. 306733). W.H. is grateful to the Austrian Science Foundation (FWF) for financial support via the SFB project IR_ON. Ehsan Hassanpour Yesaghi and Sebastian Manz are acknowledged for technical assistance in the laser lab. We thank Nadia Schwitz for help with photography of the emission from CsPbX₃ solutions, Dr. Dmitry Dirin for synthesis of CdSe and CdSe/CdS nanoplatelets and Dr. Nicholas Stadie for reading the manuscript.

Author contributions

M.V.K. conceived and initiated the work. S.Y., M.H. and W.H. performed the ASE and lasing measurements; S.Y. analysed the ASE/lasing results; L.P. and F.K. synthesized the CsPbX₃ NCs; M.I.B. collected the transmission electron microscopy images; G.D.L. and M.F. provided fs and ns laser setups and technical advice; M.V.K., W.H. and M.F. supervised the work. S.Y. and M.K. wrote the manuscript. All authors discussed the results and commented on the manuscript.

Additional information

Supplementary Information accompanies this paper at <http://www.nature.com/naturecommunications>

Competing financial interests: The authors declare no competing financial interests.

Reprints and permission information is available online at <http://npg.nature.com/reprintsandpermissions/>

How to cite this article: Yakunin, S. *et al.* Low-threshold amplified spontaneous emission and lasing from colloidal nanocrystals of caesium lead halide perovskites. *Nat. Commun.* 6:8056 doi: 10.1038/ncomms9056 (2015).



This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>

Erratum: Low-threshold amplified spontaneous emission and lasing from colloidal nanocrystals of caesium lead halide perovskites

Sergii Yakunin, Loredana Protesescu, Franziska Krieg, Maryna I. Bodnarchuk, Georgian Nedelcu, Markus Humer, Gabriele De Luca, Manfred Fiebig, Wolfgang Heiss & Maksym V. Kovalenko

Nature Communications 6:8056 doi: 10.1038/ncomms9056 (2015); Published 20 Aug 2015; Updated 23 Sep 2015

In Fig. 5d of this Article, a shaded box was inadvertently placed over the lower part of the panel during the final stages of production. The correct version of the figure appears below.

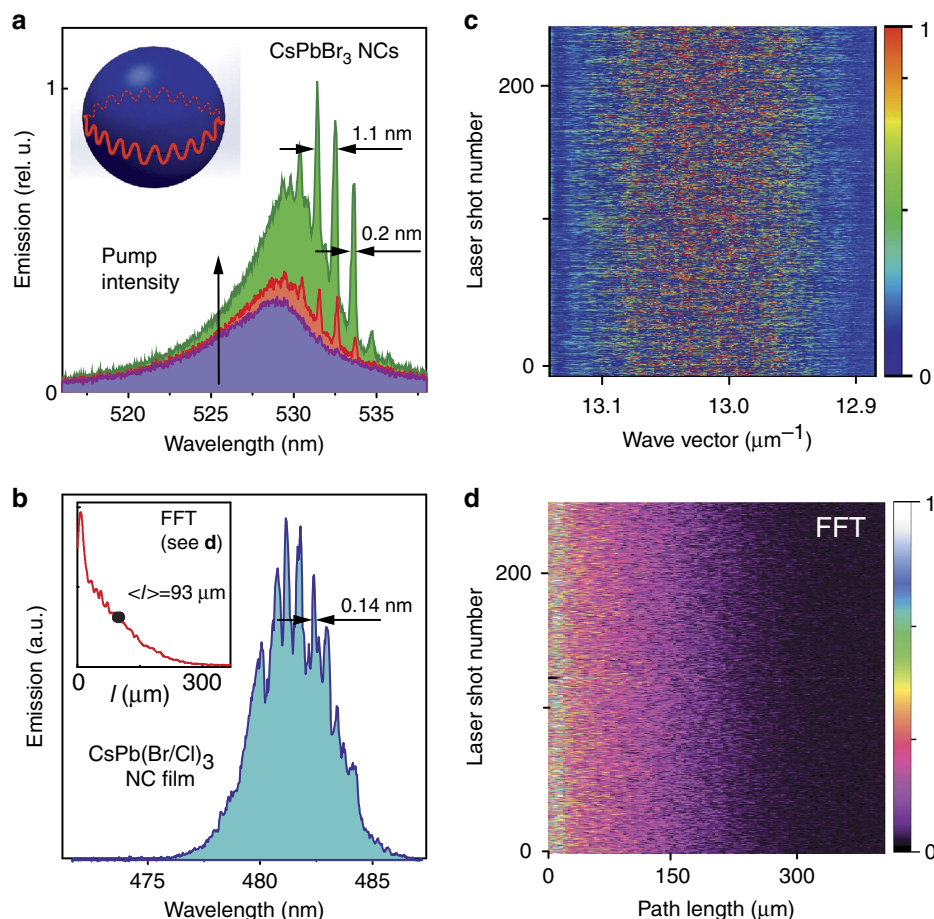


Figure 5

This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>