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Ultralow-threshold, continuous-wave upconverting lasing from subwavelength plasmons

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SUPPLEMENTAL INFORMATION

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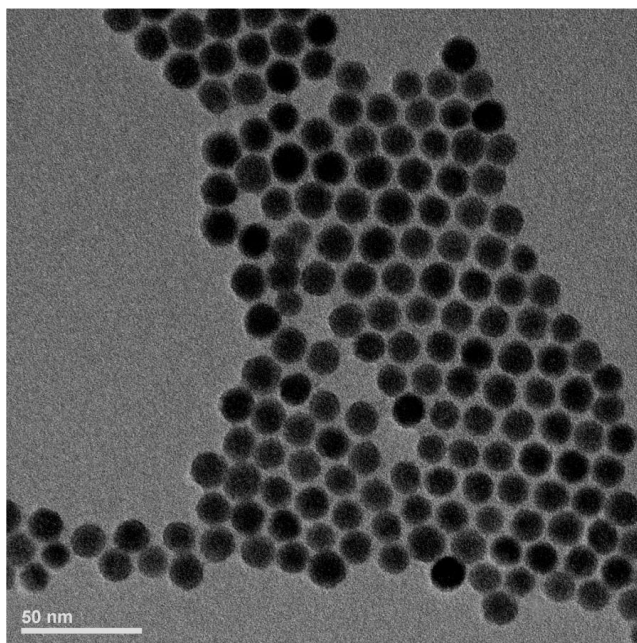


Fig. S1. Transmission electron micrograph of core/shell UCNPs.

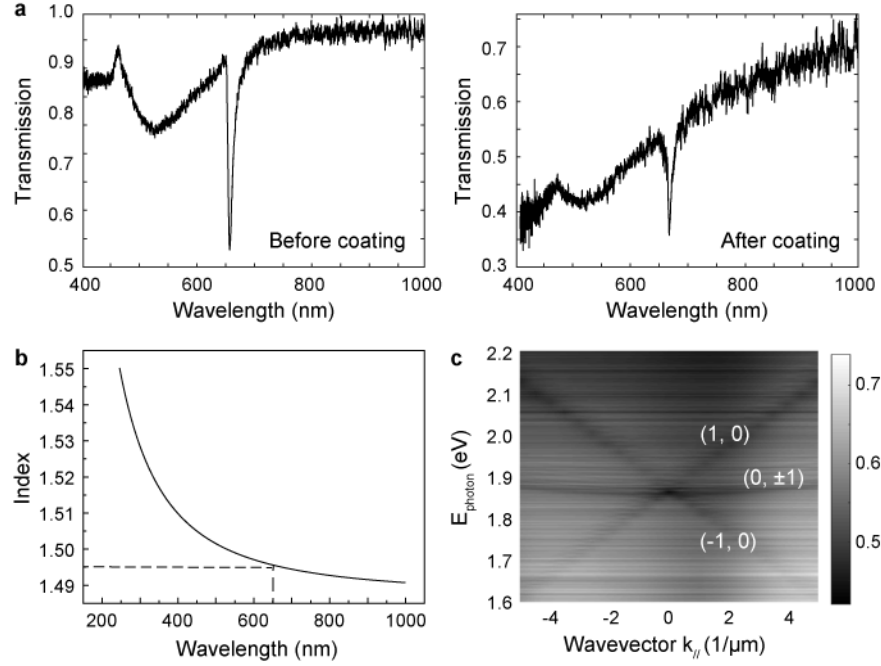


Fig. S2. Preserved lattice plasmon resonances after coating Ag nanopillars with UCNP emitters. **a**, The resonance lineshape and position of lattice plasmons showed only slight modifications after coating Ag NP arrays with $\text{Yb}^{3+}/\text{Er}^{3+}$ -based UCNPs. Measured transmission spectra of Ag nanopillar arrays with $a_0 = 450$ nm in DMSO (left) and coated with UCNPs (right). **b**, The dispersion property of a thin Er-UCNP film measured by ellipsometry, suggesting that the refractive index of Er-UCNPs is close to the fused silica substrate ($n = 1.48$) at 650 nm ($n = 1.50$). **c**, The dispersion diagram of lattice plasmons after UCNP coating shows that the plasmon resonance follows the Bragg mode defined by the lattice. The absence of Rabi splitting demonstrates that the hybrid system is in the weak coupling regime.

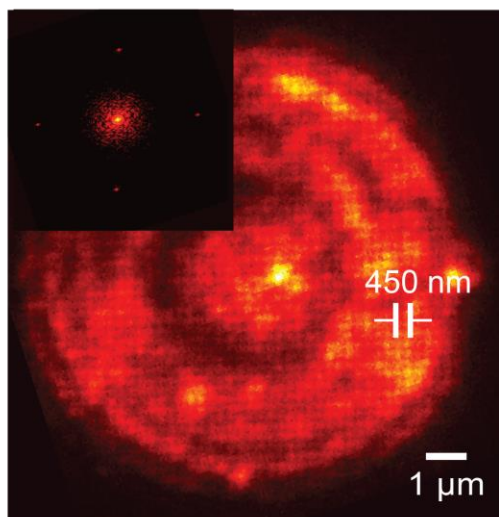


Fig. S3. Resolving plasmon-enhanced emission from UCNP-coated Ag nanopillar arrays with high numerical aperture (NA) wide-field imaging. Wide-field image of Er^{3+} upconverted red emission (ca. 660 nm) enhanced at the local plasmonic hot spots surrounding each Ag nanopillar within the array. The inset shows the fast Fourier transform of the image evidencing the periodic nature of the emission distributions. The distance between Ag nanopillars can be resolved and measured in the image; $a_0 = 450$ nm for this case. The image was collected with a $100\times$ 0.95 NA objective at 17.8 W/cm^2 .

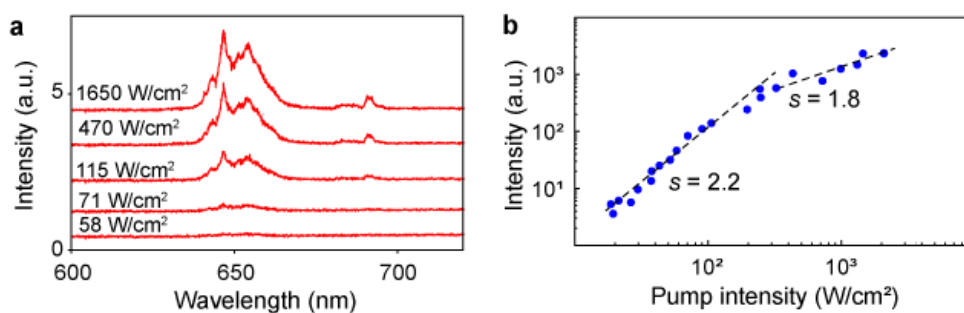


Fig. S4. Er^{3+} red-band emission and pump intensity dependence for a UCNP film. **a**, Intensity-dependent spectra of upconverted emission from the same UCNPs used in the lasing experiments. **b**, Light-in-light-out curve for the emission intensity, showing the expected nonlinear behavior typical of a pseudo 2-to-3 photon process, followed by the onset of saturation at higher pump fluences. There is no Ag nanopillar array for this control measurement.

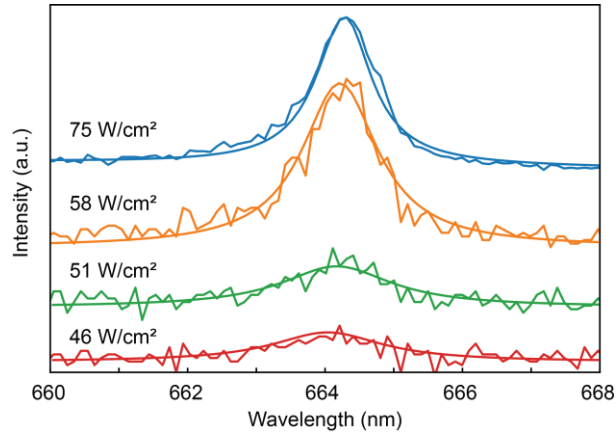


Fig. S5. Evolution of spectral linewidth as pump intensity increases beyond threshold. Zoom-in on the lasing mode shown in Fig. 1e at different excitation intensities, showing spectral narrowing as the pump increases from below to above the lasing threshold of 70 W/cm².

Table S1. Emission center wavelength and linewidth of upconverting nanolasing as the pump increases from below to above the lasing threshold. Here, x_c is the peak center wavelength; FWHM is the full-width-at-half-maximum.

Power (W/cm²)	46	51	58	75
Xc (nm)	664.08	664.24	664.25	664.29
FWHM (nm)	2.02 ± 0.16	2.01 ± 0.21	1.37 ± 0.19	1.27 ± 0.21

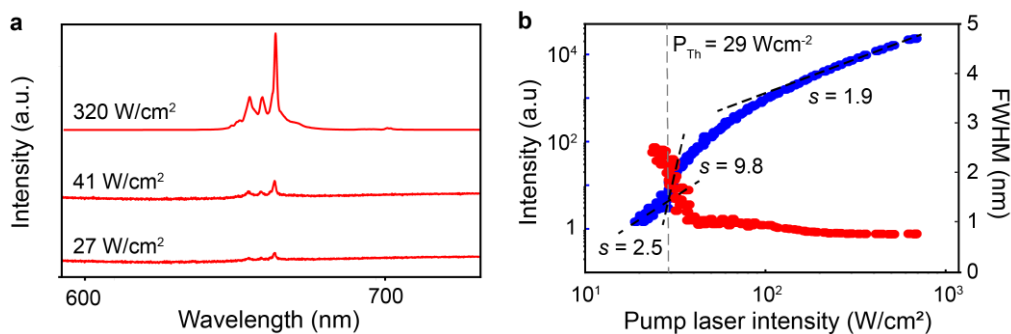


Fig. S6. Pump intensity dependence of emission mode intensity and bandwidth for Ag nanopillar arrays coated with UCNPs. **a**, Intensity dependent lasing spectra with the lasing mode peak at 664 nm. **b**, Light-in-light-out curve for the mode at 664 nm, showing nonlinear behavior with high gain and slope of 9.8, and narrowing below 1 nm width above threshold. The threshold is estimated to be 29 W/cm^2 , based on the simultaneous rapid emission intensity growth and line narrowing. This threshold, to the best of our knowledge, is the lowest threshold ever recorded for a plasmon nanolaser², and also for an upconverting nanoparticle-based laser (Supplementary Table 3).

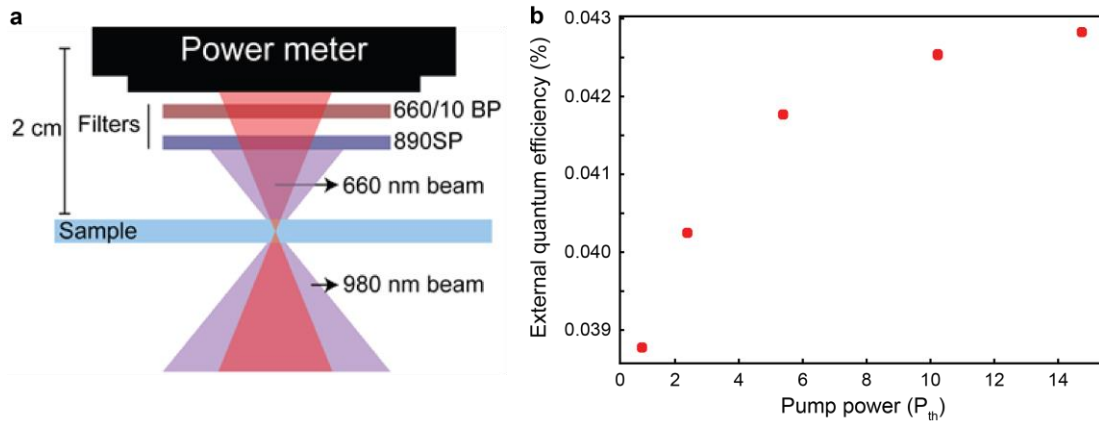


Fig. S7. Measured external quantum efficiency (EQE) of the upconverting plasmonic laser. **a**, Scheme of the experimental setup for the EQE measurements. **B**, The external quantum efficiency calculated by $EQE = \frac{P_{out}}{P_{in}}$. This value implies a Purcell enhancement of approximately > 1000 for UCNPs located within the nanolaser mode volume, slightly larger but in reasonable agreement with our measured and simulated values based on the following considerations. First, the measured UCQY for these particles is ca. 1% under moderate excitation power in solution. Second, if we assume spontaneous emission is isotropic, then for a 1-cm diameter circular detector placed 2 cm from the sample, we would expect to collect 1/64 of total emission (1.56%). Assuming 1% UCQY, then the detected P_{sp}/P_{in} is expected to be 0.0156% (assuming all input power is absorbed), where the P_{sp} is the spontaneous emission signal collected only within the solid angle of the detector (this number will actually be somewhat smaller considering that not all spontaneous emission is in the red spectral band). However, our measured EQE is 2.76 times larger than this value, which suggests that interactions with the plasmonic array cavity enhance the EQE. Importantly, only a small fraction of the UCNPs in our device are within the confined plasmonic hot spots within 25 nm around NP surface (fractional volume is $< 1/500$), which are the only places of population inversion and hence lasing³. Therefore, this small subset of UCNPs is responsible for most of the enhanced efficiency relative to the spontaneous emission value. More specifically, this implies emission into the lasing mode is enhanced by >1000 times for UCNPs within the mode volume. This agrees reasonably well with the estimates of Purcell enhancements in our devices, especially considering (i) there will be contributions from UCNPs outside the mode volume, and (ii) absorption of the pump will be enhanced within the mode volume – both of which will lead to somewhat lower enhancement estimates within the mode volume (i.e., lower than 1000).

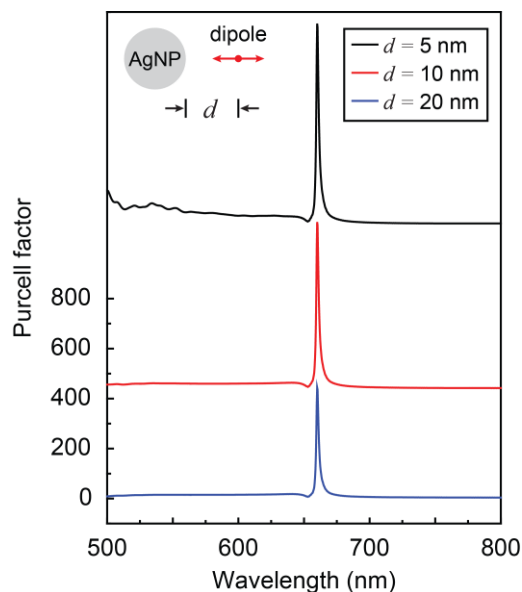


Fig. S8. The Purcell enhancement from plasmonic nanocavity arrays. The decay lifetime of Er-doped UCNPs can be considerably reduced within a photonic cavity because of the Purcell effect. We modeled the Purcell enhancement from our plasmonic nanocavity arrays by placing a dipole emitter inside the lattice unit with periodic boundary condition. By comparing the emission rate of the positioned emitter before and after coupling to a cavity, we found that the Purcell factor varies from 444, 671 to 820 for a dipolar emitter positioned at 20 nm, 10 nm and 5 nm away from the nanopillar surface. The black and red curves have offset from the blue one vertically.

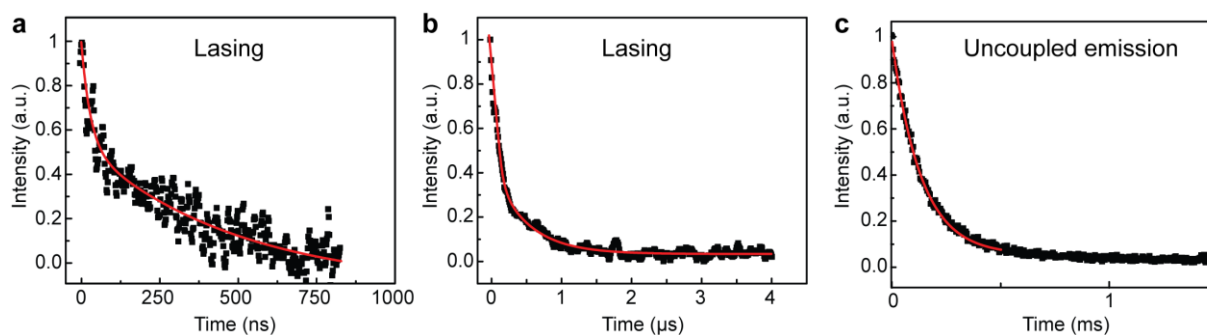


Fig. S9. Exponential fits for decay curves from a UCNP-coated plasmon nanoparticle array lasing device. **a.** A bi-exponential fit is used in panels (a) and (b): $y = y_0 + A_1 e^{-x/t_1} + A_2 e^{-x/t_2}$, and fitting values are listed in **Table S2**. The fit for the device operating above threshold shows a fast component of approx. 66 ns and a slower component of ca. 510 ns, capturing the position-dependent Purcell enhancements for Er^{3+} emitters in the plasmonic nanopillar array. The measurements were collected using a pulse selection system (Conoptic.inc) working at 100 kHz (10 μs total window) with a 10/90 duty cycle for a collection window of 1 μs . The collected wavelength range covers 655-665 nm, selected using a band pass filter centered at 660 with a span of 10 nm. The excitation intensity was 5 kW/cm^2 . **b.** The measurements were collected using the pulse selection system with a 5 μs collection window. The excitation intensity was 30 kW/cm^2 . The fit for the device operating above threshold shows similar values to those in (a): a fast component of approx. 56 ns and a slower component of ca. 486 ns, capturing the position-dependent Purcell enhancements for Er^{3+} emitters in the plasmonic nanopillar array. The slightly faster values may be attributed to the higher average pump intensity at the sample. **c.** Lifetime data with a 2 ms range from a nanolasing device below lasing threshold to evaluate the decay dynamics of the UCNPs that are not within the mode volume of the plasmonic array (majority of the UCNP film). As expected, the curve is dominated by a mono-exponential decay with lifetime of $\sim 130 \mu\text{s}$, consistent with lifetime measurements of these UCNPs when not deposited on the plasmonic array. Here, a CW pump was used, which was electrically modulated on and off every 2 ms. The temporal resolution with this scheme is approximately 3 μs .

Table S2. Lifetime values and their corresponding coefficient values for bi- and tri-exponential fits to a 660/10 nm band wavelength range (655-665 nm) luminescence from plasmonic nanocavity arrays emitting at 660 nm.

Intensity	t_1	A_1	t_2	A_2
5 kW cm^{-2} (Avg.)	66.2 ns	0.016	510 ns	2.95

30 kW cm⁻² (Avg.)	56.1 ns	0.25	486 ns	0.32
191 W cm⁻² (CW)	131 μs	0.92	N/A	N/A

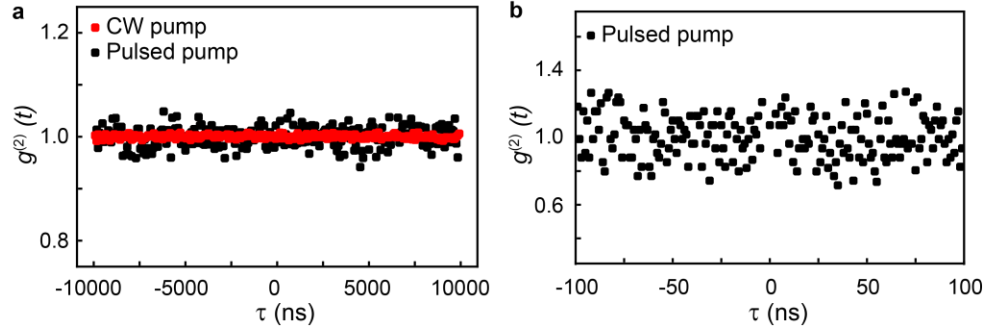


Fig. S10. Temporal coherence of upconverting nanolasing by $g^{(2)}$ measurements under CW and pulsed pump. **a**, $g^{(2)}(t)$ for 10000 ns window and bin size 100 ns for the plasmon laser at 664 nm under CW excitation above threshold (112 W/cm^2) in red, and pulsed excitation (230 W/cm^2) in black showing the values of 1 for the entire window. **b**, $g^{(2)}(t)$ for 100 ns window and bin size 1 ns for the plasmon laser at 664 nm under pulsed excitation above threshold (230 W/cm^2), showing semi-CW emission and no modulation with the 80 MHz excitation (12.5 ns delay between pulses) and with values close to 1 for the entire window.

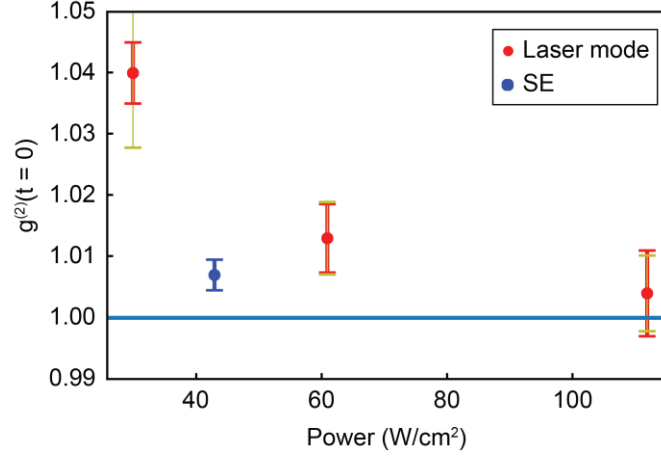


Figure S11. Second order correlation measurements from plasmonic nanocavity arrays below, near and above P_{th}, converging to 1 for above threshold pump powers. A comparison to Er³⁺ spontaneous emission (SE) from UCNPs on a glass substrate is provided (blue dot). The error bars in red were estimated by averaging the $g^{(2)}(0)$ values from 3 measurements of 8 h collection time. The yellow error bars represent the standard deviation of the noise level of each measurement. The observed trend of $g^{(2)}(0)$ values from the device (red dots) vs. pump power is consistent with expectations, where bunching behavior is expected below threshold and $g^{(2)}(0)$ approaches 1 as the pump nears threshold. The SE $g^{(2)}(0)$ value which is slightly greater than 1 (blue dot) but less than the values for sub-threshold emission from the device is also consistent with expected $g^{(2)}(0)$ for UCNPs on a substrate vs. those in a cavity.

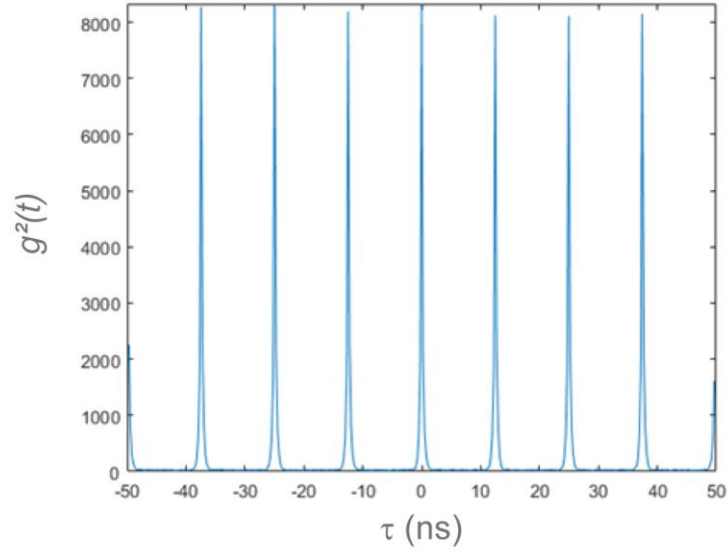


Fig. S12. $g^{(2)}$ histogram of the pulsed laser at 800 nm showing pulsing of 80 MHz (bunching rise every 12.5 ns), in 50 ns range, bin 0.25 ns. This is in contrast to the $g^{(2)}$ histogram of semi-CW plasmon lasing emission under pulsed excitation, which shows no bunching behavior (Fig. S10b).

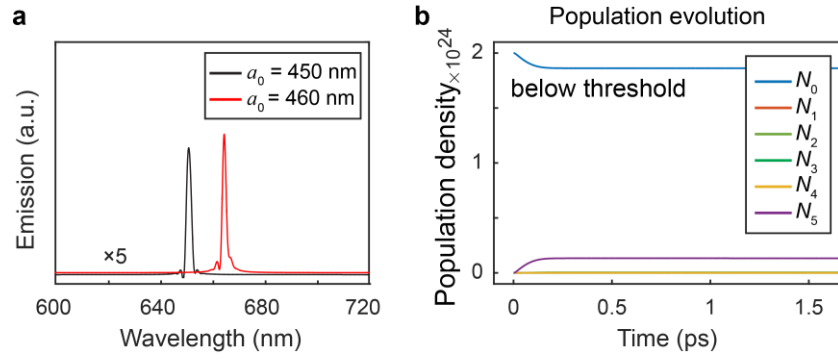


Fig. S14. Simulated emission profiles of upconverting lasing with a semi-quantum model. **a**, Simulated upconverting nanolasing showed a single-mode lasing emission with wavelength determined by the lattice constant a_0 of the array. **b**, No population inversion between different energy levels was observed in our semi-quantum simulations at a pump power of 27.2 W/cm^2 below the lasing threshold.

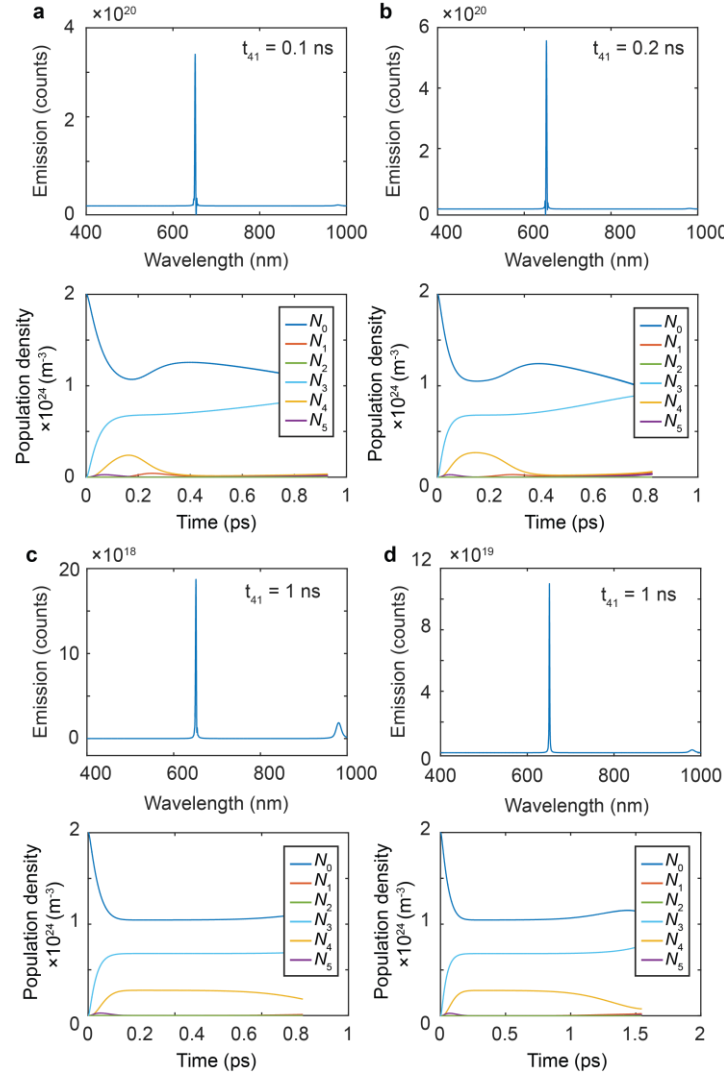


Fig. S15. The evolution of lasing buildup dynamics and emission intensity with increased transition lifetime t_{41} . Lasing emission and time-dependent population inversion for emission lifetime **a**, $t_{41} = 0.1$ ns, **b**, $t_{41} = 0.2$ ns and **c-d**, $t_{41} = 1$ ns. In the semi-quantum system, we modeled the transition lifetime $t_{41} = 0.1$ ns, which is faster than the emission lifetime (200 ns) considering the Purcell effect. The difference is primarily restricted by the limited simulation time window with the finite-difference time-domain approach, which accounts for both geometry effects from the cavity and the multi-photon population transitions for upconverting materials. With increased decay lifetime from 0.1 ns to 1 ns, the population inversion builds up more slowly, as expected, and the characteristic population transition from N_4 to N_1 for lasing happens at a later stage (panels a-c). Since the energy transition is not fully captured for the $t_{41} = 1$ ns case, lasing intensity was smaller in panel c. With a longer simulation time, the lasing emission and associated energy transition from N_4 to N_1 were recovered (panel d). Note that the intrinsic plasmon lifetime is $\sim$ fs scale, and hence the ultrafast dynamics of population inversion scale with the increased emission lifetime t_{41} ($>$ ps). Thus, we increased the transition rates in the model to elucidate the underlying photophysics in the system, especially (1) the population inversion buildup for lasing action and (2) the progression of the nonlinear rising slopes of the light-light curves.

Table S3. Summary metrics of previously reported plasmon and upconverting lasers in terms of types, pump modality, operation temperature and lasing thresholds. Our upconverting plasmon nanolasers showed the lowest lasing threshold while satisfying both continuous wave pump and room temperature operation for the first time².

*For comparison, we note when average (avg.) powers are reported for the pulsed excitation measurements, and peak power is left unlabeled. Due to the ultra-short laser pulses (fs), high repetition rate (80 MHz), and long lanthanide lifetimes that result in CW lasing despite a pulsed pump, the Table summarizes threshold values in average power as well as peak power for our UCNP-plasmon laser.

Laser type	Year	Pump (pulse length, operation frequency)	Temperature	Lasing Threshold
Plasmon nanowire-on-film laser ⁴	2009	100 fs, 80 MHz	< 10 K	50 MW/cm ²
Plasmon microdisk-on-film laser ⁵	2011	100 fs, 10 kHz	Room temperature	3000 MW/cm ²
Plasmon nanowire-on-film laser ⁶	2012	CW	Liquid nitrogen	3.7 kW/cm ²
Plasmon nanoparticle array laser ³	2013	100 fs, 1 kHz	Room temperature	1 mJ/cm ²
Plasmon nanohole array laser ⁷	2013	CW	< 150 K	5 kW/cm ²
Plasmon nanowire-on-film laser ⁸	2014	150 fs, 800 kHz	Room temperature	0.2 mJ/cm ²
UV plasmon nanowire-on-film laser ⁹	2014	10 ns, 100 kHz	Room temperature	1 MW/cm ²
Plasmon nanodisk-on-film laser ¹⁰	2017	4.5 ns, 1 kHz	Room temperature	10 kW/cm ²
Photonic UCNP microbead laser ¹¹	2018	CW	Room temperature	50 kW/cm ²
Upconverting plasmon nanolaser (this work)	2019	CW	Room temperature	29 W/cm ²
				70 W/cm ²
		150 fs, 80 MHz	Room temperature	32 W/cm ² avg.*, 2.7 MW/cm ² (peak)
				210 W/cm ² avg.*, 18 MW/cm ² (peak)
				300 W/cm ² avg.*, 26 MW/cm ² (peak)

Supplementary References

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