Silicon coupled with plasmon nanocavities generates bright visible hot luminescence

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To address the limitations in device speed and performance in silicon-based electronics, there have been extensive studies on silicon optoelectronics with a view to achieving ultrafast optical data processing1–3. The biggest challenge has been to develop an efficient silicon-based light source, because the indirect bandgap of silicon gives rise to extremely low emission efficiencies. Although light emission in quantum-confined silicon at sub-10 nm length scales has been demonstrated4–7, there are difficulties in integrating quantum structures with conventional electronics8–9. It is desirable to develop new concepts to obtain emission from silicon at length scales compatible with current electronic devices (20–100 nm), which therefore do not utilize quantum-confinement effects. Here, we demonstrate an entirely new method to achieve bright visible light emission in ‘bulk-sized’ silicon coupled with plasmon nanocavities at room temperature, from non-thermalized carrier recombination. The highly enhanced emission (internal quantum efficiency of >1%) in plasmonic silicon, together with its size compatibility with current silicon electronics, provides new avenues for developing monolithically integrated light sources on conventional microchips.

In bulk silicon, emission from hot carriers (non-thermalized carrier recombination) has been observed by injecting carriers at large applied bias10. However, the measured internal quantum efficiency is extremely low, because the hot carrier relaxation time (intraband, 0.1–1 ps) is much faster than the radiative lifetime (~10 ns)11–14, leading to very poor efficiency (~1 × 10−4) for hot luminescence across the direct band at the Γ point. However, visible light emission from hot carriers in ‘bulk’ silicon can be efficient if the radiative lifetime becomes comparable with the hot carrier relaxation time. In addition, enhanced emission from hot carriers in silicon can enable studies of photophysics of indirect-bandgap materials, which is otherwise challenging because of the intrinsic low emission quantum yields. Although silicon photonic-crystal nanocavities have recently demonstrated Purcell enhancements up to 100, the emission was mostly generated from thermalized carriers in the near-infrared wavelength range15,16. Here, we demonstrate visible light emission with high internal quantum yield (>1%) at room temperature from ‘bulk-sized’ (no quantum-confinement) silicon integrated with a plasmonic nanocavity, via the Purcell enhancement effect17,18. Highly concentrated electromagnetic fields inside plasmon nanocavities induce phonon-assisted light emission from hot carriers before their thermalization to the lowest energy state (near X-point) in the conduction band (Fig. 1a). The interaction of charged carriers with phonons and size-tunable nanocavity plasmons provides new ways to modulate the emission efficiency in silicon devices in the visible range.

To generate light emission from hot carriers, we fabricated a plasmonic nanocavity on single silicon nanowires (diameter range of 30–80 nm) by depositing a 5 nm SiO2 interlayer (to prevent recombination of carriers at the metal surface while maintaining strong nanocavity plasmon fields in the silicon), followed by a 100-nm-thick silver Ω-shaped cavity (see Methods) to support surface plasmon polariton modes (Fig. 1b–d). Room-temperature microphotoluminescence measurements were carried out on individual nanowire devices with an Ar+ laser excitation source (2.708 eV). Bright visible light emission was observed from single plasmonic silicon nanowires (Fig. 1e). Because hot carrier emission competes with intraband relaxation, a broad hot luminescence band is expected, ranging from the laser excitation to the indirect bandgap energy in silicon. Figure 1f presents broad hot luminescence spectra with high counts obtained from a single silicon nanowire coupled with a Ω-shaped cavity (silicon diameter, d = 65 nm). No observable photon counts above the background level (~100 counts) were detected from 5 nm SiO2-coated silicon nanowires (d = 60 nm) without the silver nanocavity (nanowire lengths were typically 10 μm). Furthermore, under ultraviolet laser excitation at 3.486 eV, the hot luminescence band was observed to extend to the laser excitation energy, resulting in a broad ultraviolet to visible light emission (Supplementary Fig. S1). These observations suggest that the hot carriers emit photons through a phonon-assisted recombination process during intraband relaxation. Furthermore, to test the generality of visible hot luminescence in plasmonically coupled silicon, we performed experiments on planar silicon patterned with silver bowtie structures (Supplementary Fig. S2), producing a spectrum similar to that of plasmonic silicon nanowires with hot luminescence bands.

To study the effect of size-tunable plasmonic nanocavity resonances on hot luminescence, we examined silicon nanowires of various sizes (d = 30–80 nm), coupled with a Ω-shaped cavity. We found that the intensity of the hot luminescence band (integrated counts) reached a maximum at a resonant size (d = 70 nm), with a clear peak structure reflecting phonon-assisted hot luminescence processes (Fig. 2a). To study the corresponding electromagnetic field distribution and nanocavity Purcell enhancement, numerical simulations were performed for the Ω-shaped devices (see Methods). The simulated frequency-dependent electromagnetic field intensity inside the cavity (d = 70 nm) correctly reproduces the resonance peaks observed in the hot luminescence spectrum (Fig. 2a). However, the observed photoluminescence spectrum shows more structure, which is related to the complex phonon-related carrier relaxation channels (peaks 1–5 in Fig. 3a, discussed further in the following). Simulations also reveal a plasmonic cavity mode along the silver/SiO2 interface perpendicular to the long axis of the nanowire, as shown in Fig. 2b–d. Waveguide modes propagating along the long axis cannot be supported in the plasmonic nanowires because of the high propagation losses (10–30 dB μm−1)17, which have been confirmed by

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three-dimensional simulations (Supplementary Fig. S4). For the highly confined plasmonic cavity modes, the quality factor was estimated to be ~30, together with an ultrasmall mode volume of $\lambda^3/10^6$ ($\lambda$ is the free-space wavelength), giving rise to a large radiative rate enhancement (Purcell factor of $\sim1 \times 10^5$) at 2.505 eV (see Methods), with outcoupling efficiencies comparable to photonic nanowires (Supplementary Fig. S5). The position-dependent Purcell factor map shows an enhancement of $\sim1 \times 10^3$ at <5 nm from the silicon surface, and $\sim1 \times 10^2$ enhancement throughout the majority of the nanowire core (Supplementary Fig. S6). Note that the actual emission rate is also related to frequency matching between the cavity resonance and the homogeneously broadened emitter frequencies\(^{19-21}\). To estimate the spontaneous emission rate enhancement from the Purcell factors, we calculated the enhanced rates as a function of energy mismatch between the emitter and cavity modes, for both resonant ($d = 70$ nm) and non-resonant ($d = 50$ nm) sized nanowires, and obtained a spontaneous emission enhancement of $\sim1 \times 10^3$ for the resonant size ($d = 70$ nm) near the nanowire surface (Supplementary Fig. S7). The spectral outcoupling efficiency, which resembles the spectral shape of the cavity field intensity, further modulates the emission intensity of hot luminescence (Supplementary Fig. S8), resulting in an order of magnitude higher photon counts for the resonant case (see Supplementary Section, ‘Discussion on Spontaneous Emission Enhancement’, for a detailed discussion). Such large enhancement enables hot carrier recombination before their thermalization (Fig. 1a), which would otherwise lead to poor radiative quantum yields ($<1 \times 10^{-4}$). The internal quantum efficiency for hot luminescence in plasmonic silicon was estimated to be 1.4% (see Methods), which can be further improved by optimizing the plasmonic cavity structure.

To understand the interplay of silicon phonon modes and nanocavity plasmon resonances leading to efficient light emission, we carried out polarization-dependent photoluminescence measurements. Because surface plasmon polaritons are transverse magnetic waves at the metal–dielectric interface\(^{22}\), the electric field of plasmonic cavity modes should be polarized perpendicular to the nanowire long axis. Indeed, the resonant-sized plasmon cavity ($d = 70$ nm) showed perpendicularly polarized hot luminescence bands with an emission polarization ratio $\rho$ of 0.56, where $\rho = (I_\perp - I_\parallel) / (I_\perp + I_\parallel)$ (Fig. 3a). The polarization emission bands overlap exactly with the calculated field intensity inside the cavity (Fig. 3a). However, the finer peak structures observed within the cavity resonances are more pronounced for the perpendicularly polarized...
Perpendicularly polarized hot luminescence spectra (Fig. 3b), as and phonon-assisted hot carrier emission, were observed. Low photon counts), distinct bands, attributed to cavity plasmons and emit, albeit with low counts. To ensure that the sharp peaks originate from the phonon-assisted hot luminescence bands, we measured spectra at a different laser excitation energy (2.331 eV), confirming the shift of peak (‘P’) positions (from the laser line) and the interplay between the ‘P’ and ‘C’ peaks (Supplementary Fig. S9).

Our finding is that phonon-assisted hot luminescence is greatly enhanced when the hot carriers assisted by phonons with the highest density of states are resonantly coupled with the cavity plasmons. The simulated size dependence of plasmon cavity modes (Fig. 3c) shows that the exact resonance between the three strong hot luminescence bands observed at 2.51, 2.34 and 2.18 eV and the plasmon cavity modes occurs at a silicon nanowire size of ~70 nm. This simulated prediction is further verified from the size-dependent photoluminescence spectra of nanowires with
diameters ranging from 40 to 80 nm (Fig. 3d). As the diameter approaches the resonant size of \( \sim 70 \text{ nm} \), the hot luminescence intensity is drastically increased, reflecting a perfect resonance between the hot carriers assisted by high density of states phonons and the cavity plasmons. There is also another predicted resonance (at \( \sim 55 \text{ nm} \)) between high-density phonons and cavity modes, which was also measured experimentally.

It should be noted that light emission is only possible when phonons scatter the hot carriers to the almost vertical light line (\( k \approx 0 \)). This phonon-assisted scattering process should satisfy momentum conservation, \( k' = k + q \approx 0 \), where \( k' \) and \( k \) are the momentum values of hot carriers at the light line and at the initial electronic state, respectively, and \( q \) is the phonon momentum. Thus, the hot carrier population would depend on the phonon modes with the highest density of states where phonon dispersion has almost zero slope\(^\text{23} \), where those specific phonons can scatter the hot carrier efficiently to the light line. The phonon dispersion of silicon along the (110) direction shows that the density of states is relatively high for momentum values of \( \sim 2\pi/a(0.6,0.6,0) \) for transverse optical (TO) and transverse acoustic (TA) phonons and \( \sim 2\pi/a(0.7,0.7,0) \) for longitudinal optical (LO) and TA phonons, situated between the \( \Gamma \) and \( K \) points\(^\text{24} \). Taking into account the electronic dispersion of silicon\(^\text{25} \) (Supplementary Fig. S10b), the same momentum values of \( \sim 2\pi/a(0.6,0.6,0) \) and \( \sim 2\pi/a(0.7,0.7,0) \) correspond to the strong hot luminescence bands at 2.51 and 2.18 eV, respectively. Furthermore, the hot luminescence band at 2.34 eV corresponds to the zone edge phonon at \( k \approx \pi/a(0.9,0.9,0.9) \), with a high density of states near the L-point along the (111) direction.

The absorption process upon laser excitation involves interaction with a phonon, followed by intraband relaxation of hot carriers by phonon emission (lower \( k \)-values). This can occur by either a one-phonon process involving an optical phonon near the Brillouin zone centre (\( \Gamma \)-point) with low \( k \)-values, or a two-phonon (acoustic) process with \( k \)-values with opposite signs near the Brillouin zone boundaries\(^\text{26} \). Because the density of states of TA phonons near the zone boundary is much higher than that of longitudinal acoustic (LA) phonons in crystalline silicon, as seen in their dispersion\(^\text{24} \), intraband relaxation process would be dominated by 2-TA phonons. Based on the known phonon dispersion in silicon\(^\text{27} \), the phonon-assisted hot luminescence process is explained in Supplementary Section, ‘Discussion about the Phonon-Assisted Hot-Luminescence Process’. The broadening of the peaks with increasing energy separation from the laser excitation suggests that many other phonon relaxation pathways also start to contribute.

Our work demonstrates the unique interplay of three (quasi) particle systems—carriers, phonons and cavity plasmons—which provide an interesting test bed to study complex processes and can also lead to new properties in engineered materials not found otherwise. The ability to obtain visible light emission from silicon devices, which are compatible with length scales in current electronics (\( >20 \text{ nm} \)), opens up new ways to integrate active silicon-based photonics with other conventional functionalities. Our technique can be applied to obtain light emission from any indirect-bandgap semiconductor and will be useful for the fabrication of monolithic devices utilizing optics for ultrafast data processing.

Methods

Device fabrication. Single-crystalline undoped silicon nanowires (Sigma-Aldrich) were dispersed in ethanol and transferred onto a 150-μm-thick glass substrate. A 5 nm SiO\(_2\) interlayer was deposited by atomic layer deposition (ALD) (Cambridge Nanotech) by alternating O\(_3\) and trimethylsilane, and H\(_2\)O pulses at a temperature of 150°C. An 100 nm silver thin film was coated to form an \( \Omega \)-shaped plasmonic cavity by using an electron-beam evaporator at a low deposition rate of 0.2 Å s\(^{-1} \) for the first 50 nm and 0.5 Å s\(^{-1} \) for the remaining film. Silver bowtie structures were fabricated on the silicon substrates after etching the native oxide. The silicon substrate was covered with a 5 nm SiO\(_2\) layer grown by ALD, after which bowties were patterned by electron-beam lithography followed by the deposition of a 30 nm layer silver by electron-beam evaporation.

Optical measurements at room temperature. Silicon nanowires coupled with \( \Omega \)-shaped plasmonic nanocavities were optically excited through the 150-μm-thick glass substrate using a home-built microscope equipped with a ×60, 0.7 NA objective (Nikon), with a spatial detection resolution of 500 nm. Planar silicon, with the bowtie structures, was excited from the top side. A continuous-wave argon ion laser (Coherent) tuned at a wavelength of 457.9 nm was focused to pump the individual nanowires (with a beam spot size of 2 μm on the sample) with an effective mode volume \((V_{\text{mode}})\). For ultraviolet excitation, a frequency-doubled femtosecond pulse Ti:sapphire laser (Chameleon) was tuned at a central wavelength of 355.7 nm. Photoluminescence spectra were collected using a spectrometer (Acton-SP 500i) and a cooled charge-coupled device (CCD) (Pixis 2K, Princeton Instruments) with a spectral resolution of 0.5 nm and an overall photon detection quantum yield of \( \sim 85\% \) (wavelength range, 450–750 nm).

Numerical calculations. Simulations were performed for the silicon nanowire coupled with the \( \Omega \)-shaped plasmonic nanocavity structures with a pulsed point dipole source inside the cavity, using the commercial finite-difference time-domain (FDTD) software package (Lumerical). The eigenmodes, quality factors and field intensity profiles were analysed by Fourier transforming the calculated time-domain data to the frequency domain. By performing three-dimensional FDTD simulations, the Purcell factor \((F_{\text{P}})\) was calculated by taking into account the effective mode volume \((V_{\text{mode}})\), where \( V_{\text{mode}} = a \times n \) are the free-space wavelength and refractive index, respectively\(^\text{14} \). The effective mode volume of the plasmonic cavity modes can be expressed as\(^\text{28} \)

\[
V_{\text{eff}} = \frac{|e(r)|^2 E(r) d^2 r}{|e(r)|^2 E(r) d^2 r}
\]

where \( e(r) \) is the material dielectric constant, \( E(r) \) is measured in the silicon medium at the position where a dipole emitter would experience the calculated Purcell factor, and the electric field intensity was integrated over the entire mode structure. The frequency-dependent real and imaginary parts of the dielectric function of silver were obtained by an analytical fit to experimental data\(^6 \), and the real and imaginary parts of the refractive indices of silicon and SiO\(_2\) were taken from ref. 30.

Quantum efficiency estimation. We first estimated the optical power collection efficiency in the optical-fibre coupled spectrometer and CCD, which were used for the photoluminescence measurements. By measuring the integrated counts, while taking into account the quantum yield and the sensitivity of the CCD, the collection efficiency was estimated to be 1%. From the integrated photon counts of the photoluminescence spectrum from the sample, the photoluminescence power through the objective was measured to be 0.8 nW. Three-dimensional FDTD calculations were carried out for a silicon nanowire coupled with a \( \Omega \)-shaped cavity \((d = 70 \text{ nm}, l = 8 \mu\text{m}) \) to obtain an overall far-field ouput coupling efficiency of 0.059% through the entire emission spectral range (after considering the numerical aperture of the objective), resulting in an actual power of 1.4 μW emitted from the silicon. In addition, an absorption efficiency of 1% for the same plasmonic silicon with a \( \Omega \)-shaped cavity was calculated at a laser wavelength of 457.9 nm with a 2 μm beam size (full-width at half-maximum) using the FDTD technique to fully take into account possible absorption enhancement due to the antenna effect (Supplementary Fig. S11), giving rise to an absorbed power in silicon of 100 μW at an incident laser power of 10 mW. An internal quantum efficiency of 1.4% was therefore estimated from the ratio of the emission power from silicon (1.4 μW) and the absorbed power in silicon (100 μW).

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**Author contributions**

C-H.C. and R.A. developed the concept and design of the devices. C-H.C. fabricated the devices and performed optical measurements. C.O.A. performed the numerical simulations, fabricated devices and performed optical measurements at 532 nm excitation. J.P. fabricated and carried out the emission experiments on bowtie structures. C-H.C., C.O.A. and R.A. analysed the results and wrote the manuscript.

**Additional information**

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to R.A.

**Competing financial interests**

The authors declare no competing financial interests.