Subwavelength periodic confinement can collectively and selectively enhance local light intensity and enable control over the photoinduced phase transformations at the nanometer scale. Standard nanofabrication process can result in geometrical and compositional inhomogeneities in optical phase change materials, especially chalcogenides, as those materials exhibit poor chemical and thermal stability. Here the self-assembled planar chalcogenide nanostructured array is demonstrated with resonance-enhanced light emission to create an all-dielectric optical metasurface, by taking advantage of the fluid properties associated with solution-processed films. A patterned silicon membrane serves as a template for shaping the chalcogenide metasurface structure. Solution-processed arsenic sulfide metasurface structures are self-assembled in the suspended 250 nm silicon membrane templates. The periodic nanostructure dramatically manifests the local light–matter interaction such as absorption of incident photons, Raman emission, and photoluminescence. Also, the thermal distribution is modified by the boundaries and thus the photothermal crystallization process, leading to the formation of anisotropic nanoemitters within the field enhancement area. This hybrid structure shows wavelength-selective anisotropic photoluminescence, which is a characteristic behavior of the collective response of the resonant-guided modes in a periodic nanostructure. The resonance-enhanced Purcell effect can manifest the quantum efficiency of localized light emission.

1. Introduction

Periodic perturbation of refractive index in subwavelength dimensions can boost efficiency of light emission device. Many nanophotonic structures, such as photonic crystals (PhCs), plasmonic structures, gratings, and resonators, have been demonstrated to improve the light emission efficiency through enhancing light outcoupling efficiency and spontaneous emission rate. Nanophotonic engineering can lead to narrowband and directive light emission. Chalcogenide materials with unique phase change properties have been explored for tunable thermal emission or reflection in infrared wavelength ranges. PhC waveguide has been demonstrated on thin-film chalcogenide by e-beam lithography, showing slow light and resonance-enhanced parametric nonlinear process in material. To reduce cost and improve scalability, solution-processed chalcogenide nanostructure is recently reported through solution process and self-assembling. In this work, we demonstrate the first active chalcogenide metasurface fabricated by self-assembling with tunable dimensions. The nanophotonic structure is tailored to enhance the light emission efficiency through resonance-enhanced absorption of excitation, suppressing guided mode at emission wavelength and Purcell enhancement. The 2D hexagonal chalcogenide nanorod arrays are self-assembled on a silicon template through solution processing. Silicon nanophotonic structure with a few nanometer surface roughness enables delamination of top and bottom bulk chalcogenides during solvent evaporation leaving only a filled nanorod array. Nanophotonic confinement can simultaneously manifest local photon density for enhanced emission.
resonance absorption\cite{25} and nonlinear process.\cite{26} The guided mode with a concentration in the light-emitting materials can significantly enhance the quantum efficiency of both stimulated Raman emission and spontaneous photoluminescence (PL) process, which plays a major role in the device compared to the leaky mode enhancement of light outcoupling efficiency.\cite{27–29}

2. Localized Photon and Heat Distribution in the Hybrid Metasurface

Fabrication of the light-emitting device is composed of two steps: 1) assembling the As$_2$S$_3$ nanostructures in the silicon template; and 2) local laser annealing for enhanced PL. The first step is for shaping the chalcogenide nanostructures and the second step removes the solvent-related atomic defects and induces phase transitions in chalcogenide for effective light emission.

2.1. Self-Assembled Chalcogenide Metasurface

Here we demonstrate a simple and scalable way of producing chalcogenide nanostructures, combining advanced silicon nanofabrication and solution processing. Figure 1 shows the fabrication process and scanning electron microscope (SEM) images of a self-assembled chalcogenide–silicon metasurface structures. The silicon patterns (triangular lattice) are fabricated on a 250 nm thick silicon-on-insulator device layer via ultraviolet lithography and etching for reduced disorder scattering\cite{30} (Figure S1, Supporting Information). The lattice constant of the periodic structure is 415 nm, and we vary the hole radii from 80 to 150 nm with 10 nm per step (Figure 1b). The supporting silicon oxide buffer layer is removed via buffered oxide wet etching. As$_2$S$_3$ solution is prepared by uniformly dissolving the powder into $n$-propylamine solvent according to recipes in the prior literature.\cite{14,18} The solution is then drop-casted onto the suspended silicon membrane, forming a thick As$_2$S$_3$ film on top of the Si layer. The sample is kept in the oxygen-free glove box environment for several days at room temperature to evaporate out excess solvent. As$_2$S$_3$ dissolved in alkyl amines can be described as a nanocolloidal solution consisting of flat clusters that internally retain the structure of the layer-like starting material but capped by ionic pairs of sulfide dangling bonds and alkyl ammonium molecules. Without annealing, those solvent-related atomic defect states suppress light emission from As$_2$S$_3$.\cite{14}

Due to the fluid nature of the drop-casted materials, the solution will accumulate in the hollow region\cite{13} with excess chalcogenide material above and below the silicon membrane. The sample is left in the glove box at room temperature overnight. Upon evaporating the excess solvent, the dried bulk chalcogenide cleanly delaminates from the smooth, flat silicon surface (Figure S2, Supporting Information). Our previous work shows that the room-temperature dried chalcogenide nanorods still contain solvent-related residue (C–H/N–H...
bond),[32] which can be removed by hot plate annealing (170 °C) or laser annealing.[14] Energy-dispersive X-ray spectroscopy (EDX) mapping is used to verify the chalcogenide arrays in the silicon structure (Figure S3, Supporting Information), and little residual on silicon top surface. The results show the formation of uniform As$_2$S$_3$ triangular arrays without solvent-specific composition. With limited residual from the solvent, the surface roughness of the delaminated bare silicon region is limited to be a few nanometers, as verified by atomic force microscope imaging (Figure 1c).

2.2. Localized Laser Annealing

As shown in the cross-sectional image in Figure 2a, isolated As$_2$S$_3$ nanorod arrays are self-assembled in the plane of the suspended silicon template. Laser annealing is then achieved by focusing a 532 nm continuous-wave laser onto the planar chalcogenide nanostructure. The laser spot size is about ≈1 µm. The intensity profile is superimposed onto the SEM image in Figure 2b. An example of the photothermal heat distribution in the middle of nanostructured plane (marked as a dashed blue line in Figure 2d) is shown in Figure 2c at a hole radius of 140 nm, simulated by the combination of the discontinuous Galerkin time-domain algorithm (for Maxwell equation) and finite-difference method (for heat transport equation), assuming an environmental temperature of 300 K.[33] As the excitation laser power is set at 40 µW µm$^{-2}$, the photothermal effect heats the local area to 170 °C. The laser Gaussian profile is dramatically modified by the nanostructure. The modified mode profile leads to localized heating in plane (Figure S4, Supporting Information) and out of the plane (Figure S5, Supporting Information). The cross-sectional view shows that the highest temperature is found on the interface between the metasurface and bulk chalcogenide substrate (Figure 2d). The constructive interference between incident and reflected light from metasurface–bulk substrate chalcogenide interface can result in the highest optical field on the interface. The area with highest photon density has the highest heat generation rate. Beyond phase transition temperature, extra influence from the crystallization might slightly modify the temperature distribution. The top view of the hot spot distribution on the interface between the metasurface and bulk substrate is shown in the Figure 2e. The local temperature can be up to 285 °C, which is beyond the glass transition temperature of 191.7 °C.[14] The local photothermal heating removes the amine content and reconstructs the atomic structure from As$_2$S$_3$ to As$_4$S$_4$. The atomic state is stabilized after 10 s laser exposure (Figure S6, Supporting Information). As$_4$S$_4$ exhibits higher PL intensity in the visible band, which likely comes from the loosely bound Wannier–Mott exciton in the atomic network of As$_4$S$_4$.[14] Figure 2f compares the PL spectra of bulk chalcogenide before and after laser crystallization. Enhancement factors up to 35 (gray dotted curve) are observed near 760 nm. The PL spectrum gives a major PL peak at 703 nm (1.76 eV) with 98 nm bandwidth and a minor peak at 745 nm (1.66 eV) with 30 nm bandwidth. PL spectra under different wavelength excitation are distinguished from each other, showing the multicomponent nature of the laser-crystallized As$_4$S$_4$ (Figure S7, Supporting Information).

The nanophotonic structure tailors both Raman emission and PL. The Raman emission has wavelengths close to excitation, narrowbandwidth, and is weakly influenced by defect states accelerated nonradiative recombination, and thus used for characterizing the metasurface enhancement of excitation light. PL is broadband response, and its intensity is strongly influenced by those nonradiative recombination. The PL spectra depend on the superposition of resonance-enhanced mode at excitation and emission wavelengths. By comparing the metasurface enhancement of both emissions, we can obtain insights about the light emission enhancement mechanisms.

3.1. Raman Emission and Excitation Enhancement

The frequency offset of the Raman emission to the excitation laser wavelength fingerprints the unique phonon mode of the target material. Characterization of the Raman emission illustrates the mechanism of the enhancement of excitation light through coupling into the guided mode with a mode profile that overlaps well with the As$_2$S$_3$ region. Local excitation photon density enhancement in As$_2$S$_3$ is examined by micro-Raman spectrometry. Figure 3a shows the normalized Raman spectra of chalcogenide metasurface with increasing hole radii of 70, 120, and 130 nm (with 0.5 offset for clarity). In the hybrid nanostructure, the Raman peak near 305 cm$^{-1}$ is the transverse acoustic mode in silicon. The Raman peaks at 345 cm$^{-1}$ represent asymmetric stretching vibrational modes of the As$_2$S$_3$ pyramids. The relative Raman peak intensity ratio of the As$-$S bond and silicon increases with hole radius ($R$). The enhancement of the 532 nm photon excitation initially increases with $R$, and then decreases as the $R$ becomes larger than 140 nm ($R/a = 0.337$). At $R = 140$ nm, the incident photon has the highest overlap factor/enhancement factor with the chalcogenide area (Figure 3b,c), and thus, the highest Raman peak intensity. The insets of Figure 2b show the top (left) and cross-sectional (right) views of the photon distribution in the hybrid nanostructure at $R = 140$ nm, simulated by the finite-difference time-domain method (FDTD). The total enhancement factor of an exciting photon is defined as the integral of the local electric field enhancement $(F_{\text{Ex}}(\lambda_0, r))$ over the chalcogenide region:

$$\int |F_{\text{Ex}}(\lambda_0, r)|^2 dr,$$

where $\lambda_0$ is the wavelength of the excitation laser and $r$ is a vector of position. The field enhancement factor is calculated by the integral

$$\frac{1}{4\pi}\int |F_{\text{Ex}}(\lambda_0, r)|^2 |F_{\text{Em-Raman}}(\lambda, r)|^2 dr,$$

where $F_{\text{Em-Raman}}$ is the Raman emission enhancement factor. The enhancement of the Raman emission wavelength is similar to the excitation, as their wavelength is closely spaced. The trend of simulated Raman emission intensity versus hole dimension (gray circles linked by the dashed line in Figure 3b) aligns well with the experimental data (blue dots with error bars in the same figure).

3.2. Photoluminescence from the Nanostructured Chalcogenide Emitter

3.2.1. Modeling Metasurface-Modified PL Spectrum

Different from narrowband ultrafast Raman emission (femtosecond scale lifetime), PL is a nonparametric and broadband quantum process (nanosecond scale lifetime). The emission bandwidth usually is across a few photonic guided/leaky modes. Selective enhancement of emission only occurs at resonance-enhanced wavelengths. The resonant mode can effectively enhance the local density of states (LDOS), $\rho$, and thus, the spontaneous emission rate for radiative recombination. The local spontaneous emission rate is defined as

$$\Gamma_s = \frac{2\pi}{\hbar} \langle d \cdot \vec{E} \rangle^2 \rho,$$

where $d$ is the electric dipole moment, $E$ is the local electric field, and $\rho$ is the density of the electromagnetic modes or LDOS. LDOS $\rho(\lambda, r)$ can be obtained through 3D FDTD simulation. The internal quantum efficiency of the PL is $\eta = \Gamma_s / (\Gamma_s + \Gamma_{\text{nr}})$, where $\Gamma_s$ and $\Gamma_{\text{nr}}$ are the radiative and...
nonradiative recombination rates. The carrier recombination time (1/Γnr) of the chalcogenide semiconductor nanomaterial is usually at the picosecond scale, which is three orders of magnitude smaller than the radiation recombination lifetime (1/Γr). Because the quantum efficiency of the amorphous material is usually small (Γr ≪ Γnr), η (=Γr/Γnr) linearly increases with Γr. The local enhancement factor (FEm(λ, r)) of the electric field for the emitted photon is ρ/ρ0. ρ0 is the LDOS in bulk. The overall emission intensity from the arsenic sulfide emitter is given by Equation (1), assuming the intensity of light is well below the saturation level

$$\frac{I_{\text{ph}}}{I_{\text{bulk}}} = C \int_{\lambda_0,\lambda_0} |F_{\text{Ex}}(\lambda_0, r)|^2 \times |F_{\text{Em}}(\lambda, r)|^2 \times \text{EE}(\lambda, r) \, dr$$

where C is a constant describing the dipole alignment to the guided modes (0 < C < 1); FEx and FEx are the enhancement factor of the local electric field for emitted (from 600 to 800 nm) and pump/excitation (532 nm) light, respectively; λ and λ0 are the wavelengths of emission and pump light. EE(λ, r) is the optical power extraction efficiency of the local dipole emission, depending on the quality factor matching of intrinsic and outcoupling quality factors of the mode and wavelength detunings to its resonant wavelength.[2]

3.2.2. Contributions from Field Enhancement Effect and Light Outcoupling Efficiency

In the hybrid metasurface, it is important to differentiate and understand individual contributions from the local field enhancement effect (FEmFEx) and extraction efficiency (EE). Here we compare the experimentally measured PL from the metasurface with increasing hole radius and FDTD calculations of outcoupling efficiency and field enhancement factors (Figure 4). The measured PL spectra of seven devices with consecutively increasing hole radius are plotted in Figure 4a (solid red line), compared to the line shape of PL from bulk (same as the one in Figure 2f). The PL intensity is normalized to the Raman signal of the As−S−As at 325 cm−1, to ensure that the normalized PL is proportional to the quantum efficiency and excludes effect from sample uniformity and changing filling factors, etc. Comparing the PL from devices with increasing hole radii, we observe that the PL efficiency increases with hole radius, and the resonance-enhanced modes (highlighted by dashed gray curves) are blueshifted. The experimentally measured values align well with the trend of field enhancement simulated by FDTD simulation. Figure 4b plots the radius-dependent outcoupling efficiency within 15° to the Gamma point, which is correspondent to the band diagrams (Figure S8,

Figure 4. Collective PL near Γ point. a) PL spectra of the metasurface emitters with the hole radius from 80 to 140 nm in the step of 10 nm. The gray dashed curve marks the shift of modes. The PL spectra from nanoemitter embedded in metasurface (red solid curves) are compared to the line shape from the thin film (gray solid curves). b) FDTD simulation of the optical power extraction efficiency of local dipole emission embedded in planar metasurface with the hole radius as in panel (a). The trend of mode resonance shift with radius is highlighted in black dashed lines for guiding eyes. c) The product of enhancement factors of the local electric field in nanoemitter: $\int_{\lambda_0,\lambda_0} |F_{\text{Ex}}(\lambda_0, r)|^2 \times |F_{\text{Em}}(\lambda, r)|^2 \, dr$. The trend of geometry-dependent modes is highlighted by dashed white lines.
Supporting Information). As the dipole is confined in the chalcogenide region, the increased hole radius shifts those resonance-enhanced modes to longer wavelengths. The trend of the field enhancement factors is opposite, as plotted in Figure 4c, which incorporates the mode overlap among excitation, emission, and As$_4$S$_4$ region (Figure S9, Supporting Information). Thus, we conclude that the PL enhancement is dominated by the contribution from local field enhancement.

Among all the PL measurements, the maximum enhancement is achieved at a hole radius of 140 nm at the wavelength of 670 nm, where both excitation and emission resonance modes are excited, along with good mode overlap with the As$_4$S$_4$ region. We compare the FDTD-calculated spectra and experimental measurement in Figure 5a. The blue solid curve shows the experimental measurement of the chalcogenide metasurface, and the black solid curve shows the FDTD-simulated spectrum. Major spectral features are resembled in the simulation, including major peaks near 670, 700, 800 nm, and ripples around 600 nm. The bulk contribution from the chalcogenide under the metasurface plane is marked via the blue dashed curve. Comparing the metasurface PL (solid blue curve) and bulk PL (blue dashed curve), a 4x enhancement is observed with field enhancement in the nanostructure.

### 3.2.3. Directional PL

All the measurement and FDTD simulations are made near the Gamma point (Figures 4 and 5a). Then we explore the polar angle dependence of the PL. We measure the polar angle-dependent Raman and PL spectra. The PL is also observed to be highly directional. The Raman scattering of As=5–As varies little at an increasing tilting angle, with little influence from the nanophotonic structure. The red stars and blue crosses in Figure 5b represent Raman scatterings from As$_4$S$_4$ and silicon, respectively. In contrast, the PL intensity rapidly decreases with the incident angle, which drops to less than 10% at 8° tilting/polar angle. The empty gray squares, circles, and dots in Figure 5b mark the relative intensity of the three peaks on the As$_4$S$_4$ PL spectra. The directional PL can be attributed to metasurface nanostructure. As a control sample, a uniform thin chalcogenide film on silicon is examined with exact laser crystallization and measurement procedures as for metasurface samples. Only a 5% variation of the PL intensity is observed within 8° of sample rotation in tilting/polar angle.

### 4. Conclusion

In conclusion, we present analytical and experimental investigations of self-assembled and laser-crystallized chalcogenide nanoemitters embedded within silicon template. Near-bandgap illumination is used to initiate localized laser crystallization (high power) and to probe the Raman and PL (low power). We first quantify the enhancement of photon density at excitation wavelength through micro-Raman emission. A model incorporating excitation enhancement, Purcell factor, and extraction efficiency is compared to experimentally measured PL spectra from the nanostructured As$_4$S$_4$ emitter. The relation between peak wavelength shift and the rod dimension indicates that the PL enhancement is dominant by the Purcell effect. The overall PL enhancement is attributed to the spatial overlap between the photonic-guided modes at excitation and emission wavelengths.

### 5. Experimental Section

**Device Fabrication:** The silicon device was manufactured in a complementary metal–oxide–semiconductor (CMOS) foundry. Deep-ultraviolet lithography defines the template features on intrinsic silicon-on-insulator substrates, followed by reactive ion etching.[29] The dimension of the nanostructured area was 20 µm by 200 µm, which was much larger than the laser spot size. The finely grounded As$_4$S$_4$ dissolved in n-propylamine for highly concentrated solutions (0.4 g mL$^{-1}$). The high concentration improves the viscosity and thus changes the flow properties of the solution. The concentrated solution was then drop-casted onto a silicon template and dried, forming the self-assembled of As$_4$S$_4$ in the periodic voids.

**SEM images** were taken with a Quanta 200 FEG environmental SEM at 5 keV in high vacuum mode. Electron diffraction X-ray equipped with SEM was then used for material composition analysis (Figure S3, Supporting Information).

**Optical Measurements:** The chalcogenide metasurface was characterized by Raman spectra and PL. Raman spectra were collected by coupling the light scattered from the sample to an inVia Raman...
spectrometer through a ×20 objective, with an ≈1 μm² laser spot size and 0.2 numerical aperture (Renishaw). The excitation wavelength was set at 532 nm.

Numerical Simulation: The simulation of excitation mode enhancement was carried out by forwarding design. A plane wave of 532 nm light was normally incident onto the metasurface plane. The broadband emission mode profile was performed by inverse design. A dipole source covering the light emission bandwidth of chalcogenide was placed above the metasurface plane. The spectral response in chalcogenide region was collected and summarized at four random locations the source placed. The spatial resolution was set at 5 nm. The material absorption and dispersion of the silicon and chalcogenide were separately measured and taken into consideration in simulation.

The extraction efficiency of the local dipole emission and the field enhancement factors in Equation (1) were simulated using the commercial software Numerical FDTD solutions. To calculate the power extraction efficiency near the Gamma point, a dipole was set in the central hole of the metasurface in the model. The power was collected by a point monitor right above the central hole. Then the power spectrum was normalized to the spectrum of the dipole source in the model. To calculate the field enhancement factors, first a Gaussian source of 532 nm was set above the central hole of metasurface as the excitation light, and a monitor was set to get the field profile inside the 3D photonic nanostructure. Then in another model, several Gaussian sources were set in the holes as emitters to get the field distribution profile of emission light.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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