Engineering Directionality in Quantum Dot Shell Lasing Using Plasmonic Lattices

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ABSTRACT: We report how the direction of quantum dot (QD) lasing can be engineered by exploiting high-symmetry points in plasmonic nanoparticle (NP) lattices. The nanolaser architecture consists of CdSe−CdS core−shell QD layers conformally coated on two-dimensional square arrays of Ag NPs. Using waveguide-surface lattice resonances (W-SLRs) near the Δ point in the Brillouin zone as optical feedback, we achieved lasing from the gain in CdS shells at off-normal emission angles. Changing the periodicity of the plasmonic lattices enables other high-symmetry points (Γ or M) of the lattice to overlap with the QD shell emission, which facilitates tuning of the lasing direction. We also increased the thickness of the QD layer to introduce higher-order W-SLR modes with additional avoided crossings in the band structure, which expands the selection of cavity modes for any desired lasing emission angle.

KEYWORDS: lattice plasmons, surface lattice resonances, waveguide, band structure engineering, colloidal quantum dots, laser directionality

Colloidal quantum dots (QDs) are attractive gain materials for coherent light sources. Unlike epitaxial semiconductors that require complex deposition steps, these nanocrystals can be solution-processed, and compared to dye molecules, they exhibit high photoluminescence quantum yields and long-term photostability. Stimulated emission from QDs has previously been a challenge due to nonradiative Auger losses, where electron−hole recombination energy is transferred to a third charge carrier instead of being emitted as a photon. To suppress Auger rates, core−shell geometries are widely used because a shell consisting of a wider-bandgap material enables spatial separation of the electrons and holes across the QD with weakened carrier coupling. Besides enhancing the optical gain of the core material, large shell volumes (>10 monolayers) can also show stimulated emission. Lasing has been demonstrated from both QD cores and shells using different cavity architectures, including ring structures, dielectric microspheres, photonic crystals, and plasmonic block reflectors, however, tuning of the direction of QD lasing is lacking.

Engineering the direction of lasing beams is important for laser projection displays, remote sensing, and on-chip optical interconnects. Diffractively coupled plasmonic nanoparticle (NP) arrays support surface lattice resonances (SLRs) whose photonic band structure can be manipulated by various design parameters including the refractive index environment, lattice geometry, and NP size. When combined with gain media, plasmonic lattices can provide optical feedback for lasing with directional emission. Although lasing emission at off-normal angles has been shown in NP superlattices, finite lattices, and honeycomb lattices, the available tuning range is small (Δθ < 3°) in these designs because of limited access to band-edge modes. Expanding the types of plasmonic modes available for optical feedback is necessary for wide-range control of lasing directionality. Since a closely packed QD layer can function as an optical waveguide, integrating QDs with plasmonic lattices may provide a route to design cavity modes through both array symmetry and waveguide architectures.

Here we show how QD lasing directionality can be engineered by exploiting high-symmetry points in plasmonic NP square lattices. We built QD nanolasers by conformally coating CdSe−CdS core−shell QDs on a 2D Ag NP array. Near the Δ point of the square lattice, hybrid waveguide-surface lattice resonance (W-SLR) modes facilitate lasing emission at off-normal angles. The lasing beams are...
azimuthally polarized with a donut shape because of the optical feedback from the sidebands of the W-SLR modes. By varying the periodicity of the plasmonic lattices, we tuned other high-symmetry points (Γ or M) to overlap with the CdS shell emission to control different lasing angles. Finally, we increased the thickness of the QD film to access higher-order W-SLR modes with avoided crossings in the photonic band structure, thereby expanding the selection of cavity modes to realize any desired lasing emission angle.

Figure 1a depicts a laser architecture consisting of a CdSe–CdS QD waveguide layer on an Ag NP lattice. First, we fabricated 2D square arrays of Ag NPs (spacing \(a_0 = 400 \text{ nm}\), diameter \(d = 70 \text{ nm}\), height \(h = 60 \text{ nm}\)) on fused silica using solvent-assisted nanoscale embossing (SANEM) and PEEL processes.\(^{36,37}\) Second, we synthesized biaxially strained, core–shell QDs\(^{40}\) with \(\sim 3.2 \text{ nm}\) diameter cores and \(\sim 15.7 \text{ nm}\) diameter shells (Figures S1 and S2) that we spin-cast on the NP lattices into a densely packed film. The large volume of the CdS shells compared to the CdSe cores resulted in strong shell photoemission at \(\sim 520 \text{ nm}\) under high pump powers (Figure S3). Next, we placed a slab of poly(dimethylsiloxane) (PDMS, \(n \sim 1.43\)) on top of the QD film as a protective layer to ensure mechanical robustness of the QD film surface. The high refractive index of the QD film \((n \sim 1.95 \text{ at } 520 \text{ nm})\) (Figure S3) and high film thickness \((90 \text{ nm})\) (Figure S4) ensured that the QD layer functioned as an optical waveguide. Coupling of waveguide modes in the QD layer and SLRs in the Ag NP lattice produced W-SLR modes (Figure 1b and Figure S5). The hybrid modes are indexed as \(W_{\text{TE}/\text{TM}}\text{-SLR}(m_1, m_2)\), where \(W_{\text{TE}/\text{TM}}\) refers to transverse electric (TE) or transverse magnetic (TM) mode of the zero-order waveguide mode and \((m_1, m_2)\) indicates the Bragg diffraction orders of the lattice. The reciprocal vector \(G\) is given by \(G = m_1b_1 + m_2b_2\), where \(b_1\) and \(b_2\) are the primitive vectors of the reciprocal lattice. In the Brillouin zone, the high-symmetry point \(\Delta\) is defined as the middle point between the \(\Gamma\) and \(X\) points with \(k_{\|} = \frac{\sqrt{3}}{4}b_1\) (Figure 1b, Figure S5). Based on the empty-lattice dispersion relation \(k_{\|} + G = n_{\text{eff}}\omega/c\), three diffraction modes \((-1, 1), (-1, -1), (1, 0)\) are degenerate in energy at the \(\Delta\) point. We designed the plasmonic NP lattice and QD film thickness using finite-difference time-domain (FDTD) simulations to overlap this \(\Delta\) point energy with the CdS QD shell emission \((500–530 \text{ nm})\) (Figure S5). Near the \(\Delta\) point, \(\omega_{\text{TE}-\text{SLR}}\), \(\omega_{\text{TM}-\text{SLR}}\), and \(\omega_{\text{WTE}-\text{SLR}}\) are produced at excitation angles of 17.5 and 20.5° \((\lambda \approx 520 \text{ nm})\) with high quality factors \((Q \sim 260)\) (Figure 1c). Because these resonances are at the two opposite sides of the \(\Delta\) point in \(k\) space, we denote these modes as \(W_{\text{TE}}\text{-SLR}\) sidebands.

To determine in more detail how the sidebands of the \(W_{\text{TE}}\text{-SLR}\) mode near the \(\Delta\) point support lasing, we photoexcited QD-plasmon NP devices using 35 fs, 400 nm laser pulses at...
room temperature and collected the emission spectra at 19° (Figure 2a). At lower pump intensities (<1 mJ/cm²), the collected emission yielded only a modified photoluminescence (PL) profile (full-width-at-half-maximum (fwhm) ~5 nm) from the CdSe QD core (Figure 2b). Above a critical pump intensity (>1 mJ/cm²), a sharp and intense emission peak (λ = 515 nm, fwhm = 1 nm) from the CdS shell appeared close to the wavelength of the sidebands (λ = 520 nm, fwhm = 2 nm) (Figure 2c). Pump energy density versus output intensity curves (plotted on a log–log scale) showed characteristic lasing threshold behavior with a marked change in slope around 1 mJ/cm² (Figure 2c). As a control experiment to verify the importance of the plasmonic NP lattices for optical feedback in the hybrid W-SLR mode, we spin-cast a QD film with the same thickness on a fused silica substrate and placed a PDMS slab on top. Without the Ag NP lattice, only amplified spontaneous emission with a larger line width (fwhm ~20 nm) and lower intensity was observed from the CdS shells (Figure S7). We note that, although the emission wavelength of the CdSe core overlaps with the W-SLR mode at the Γ point (Figure 1b), we did not observe lasing from the core because the small size of the core (3.2 nm in diameter) could not provide enough optical gain to overcome the cavity loss. Figure 3a shows a photograph of the lasing emission, where we placed white paper in front of the QD laser device to capture the four emission beams. Four lasing spots were observed because of the four Δ points along the lattice axis in the ±x and ±y directions (Figure 3b). Mapping the pattern of one lasing spot using a camera-based beam profiler revealed a donut-shaped emission with small divergence angle (<2°) (Figure 3c). To investigate the polarization of the lasing mode, we captured the emission pattern at selected polarization directions by inserting a linear polarizer in front of the detector (Figure 3d). At all rotations of the polarizer, the images showed two lobes aligned perpendicular to the polarizer orientation, which indicates that the lasing signals were azimuthally polarized. To determine how the W-SLR sideband modes enable this polarization-dependent lasing, we simulated the optical band structure using the FDTD method. By varying k∥ in the θ and ϕ directions near the Δ point, respectively, we found that the W TE-SLR sidebands are excited under s-polarized light along θ and under p-polarized light along ϕ (Figure S8). Because these sideband cavity modes determine the angle and polarization of the amplified photons, lasing exhibits azimuthally polarized beam profiles. Since the symmetry at the Δ point enables W-SLR sideband modes for off-normal lasing, we further investigated other high-symmetry points in the reciprocal lattice. To achieve emission normal to the surface, we focused on the Γ point in the center of the Brillouin zone. We kept the thickness of the QD film similar to that of the Δ point studies (t ~ 90 nm) such that the wavelengths of the W-SLR modes were only determined by the diffraction conditions of the lattice. Reciprocal space analysis shows that four diffraction modes (0, ±1) and (±1, 0) are degenerate at the Γ point (|k∥| = 0) (Figure 4a,b). With a0 = 400 nm, sidebands of the W TE-SLR(1, 0) and W TE-SLR(−1, 0) modes formed near the Γ point (|k∥| = 0) around 650 nm (Figure 1b). To exploit the Γ point as optical feedback, we decreased a0 to 300 nm, which shifted these sidebands to a shorter wavelength range to overlap with the CdS shell emission (Figure 4c and Figure S9). We found that the W-SLR

Figure 2. Coherent lasing action from sidebands of the W-SLR mode near the Δ point. (a) Scheme of lasing measurement. (b) Power-dependent spectra at 19°. The inset schemes of QDs represent the core emission at low pump intensity (<1 mJ/cm²) and the shell intensity as a function of input pump pulse energy on a log scale. (c) Output emission intensity as a function of input pump pulse energy on a log–log scale.

Figure 3. W-SLR sidebands provided optical feedback for four azimuthally polarized lasing beams. (a) Photograph of four lasing spots. (b) Scheme of lasing emission angles and polarization. The green circles show the lasing beams, and the arrows indicate the polarization direction. (c) Far-field emission profile of one lasing spot. White arrows indicate the polarization direction of the output lasing pattern. (d) Beam profiles under selected polarization directions. White arrows show the polarization direction of the linear polarizer in front of the detector.
modes near the Γ point support lasing normal to the plane of the NP lattice. The emission profile was stretched along the lattice axes because these W-SLR sidebands (Figure S9) are less dispersive than the sidebands near the Δ point (Figure 1b). We found that the emission pattern has a donut shape, which additionally confirms that the sidebands of the W-SLR modes provide optical feedback (Figure S9).

To expand the range of lasing emission angles, we took advantage of the high-symmetry point M at the boundary of the Brillouin zone for lasing. Because the energies of the diffraction modes are proportional to $|k_\parallel + G|$, the eight...
diffraction modes \((1, 0), (0, 1), (1, -1), (-1, 1), (0, -2), (-2, 0), (-1, -2),\) and \((-2, -1)\) are degenerate at the M point where \(k|| = \frac{1}{2}k_1 + \frac{1}{2}k_2\) (Figure 4d,e). With \(a_0\) increased to 500 nm, the sidebands of the W-SLR mode near the M point overlap the CdS shell emission, resulting in lasing emission at 45° (Figure 4f and Figure S10). Because of the 4-fold symmetry of the Brillouin zone in the square lattice, lasing showed four emission beams along the diagonal axes of the lattice (Figure S10). We note that the donut-shaped emission profile (Figure S10) was not captured in the angle-resolved emission measurement because of the large collection angle of our detector (~3°). Also, the slight mismatch between the measured lasing energy and calculated band crossing based on the empty-lattice approximation (Figure 4c,f) is from small variations in effective refractive index because of slight differences in QD film thicknesses.

Although the number of the high-symmetry points in a lattice is limited, tunable laser emission angles can be realized by manipulating the optical band structure through waveguide modes. Since the thickness of the QD film can modulate the effective refractive index of the waveguide mode,\(^{44}\) the wavelengths of W-SLR modes can be controlled. Similar to the \(\Delta\) point studies in Figure 1, we kept the periodicity constant \((a_0 = 400 \text{ nm})\) and only changed the thickness of the QD film from \(\sim 100\) to \(\sim 200\) nm to increase the effective refractive index of the waveguide mode.\(^{44}\) The wavelengths of W-SLR modes can also enable hybridization of high-order waveguide modes and SLR modes; simulated W-SLR waveguide-lattice plasmon system enables opportunities to control strong light–matter interactions for nonlinear optics, photocatalysis, and other optical processes. Moreover, the engineered band structure in this hybrid waveguide-lattice plasmon system enables opportunities to control strong light–matter interactions for nonlinear optics, photocatalysis, and other optical processes. 

**ASSOCIATED CONTENT**

Supporting Information

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Optical properties of the biaxially strained QDs in solution; optical properties of the closely packed QD thin film; thickness of the QD film; hybridization of waveguide modes and SLR modes; simulated W-SLR sidebands near the \(\Delta\) point; emission from the QD waveguide without Ag NP lattices; excitation conditions of the W-SLR sidebands near the \(\Delta\) point; band structure and lasing emission properties near the \(\Gamma\) point; band structure and lasing emission properties near the M point; lasing emission properties from the high-order W-SLR modes (PDF)

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Notes

The authors declare no competing financial interest.

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