Probing light emission at the nanoscale with cathodoluminescence

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Nanoscale optical tomography with cathodoluminescence spectroscopy

Tomography has enabled characterization of the Earth's interior, visualization of the inner workings of the human brain, and three-dimensional (3D) reconstruction of matter at the atomic scale. For tomographic techniques that rely on optical excitation or detection, diffraction generally limits the attainable resolution. In this chapter we introduce a tomographic technique, cathodoluminescence (CL) spectroscopic tomography, to probe optical properties in three dimensions with nanometer-scale spatial and spectral resolution. We first obtain two-dimensional CL maps of a 3D nanostructure at various orientations. Then, we use the method of filtered back projection to reconstruct the CL intensity at each wavelength. The resulting tomograms allow us to locate regions of efficient CL in 3D across visible and near-infrared wavelengths, with contributions from material luminescence and radiative decay of electromagnetic eigenmodes. The experimental signal can be further correlated with the radiative local density of optical states in particular regions of the reconstruction. We demonstrate how CL tomography can be used to achieve nanoscale 3D visualization of light-matter interactions by reconstructing a 3D metal-dielectric nanoresonator.
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8.1 Introduction

Tomography enables the determination of a three-dimensional (3D) function from two-dimensional (2D) data. Originally driven by the need for a non-invasive technique to peer inside the human body, the development and application of tomography has had a significant impact on a wide range of disciplines, from medical diagnosis [265] to oceanography [266] and seismology [267]. While conventional tomographic techniques yield 3D structural or chemical information with macroscopic resolution, recent advances in electron microscopy have enabled nanoscale reconstruction of material geometries [268–271]. Notably, electron tomography has been used to reconstruct nanoparticles with atomic-scale resolution [272, 273] and to identify their different chemical constituents in three dimensions [274–277].

Still, optical tomography with subwavelength, nanometer-scale resolution remains a significant challenge. For example, while super-resolution techniques can yield 3D maps of molecular structure [278, 279], they rely on fluorescent tagging and cannot probe intrinsic radiative optical properties of the nanostructure. Nearly all other label-free techniques for probing nanoscale light-matter interactions are inherently 2D: scanning a physical probe such as a nanoscale tip [76, 280–282] or fluorescent emitter [283–287] over an object creates a planar map of the optical modes or local density of optical states (LDOS). Similarly, a focused electron beam can act as a spatially-localized but optically broadband impulse excitation to an object [92, 124, 141, 142, 183, 288], but has historically been used to probe electromagnetic modes in 2D. Capturing the often complex 3D nature of light-matter interactions with nanometer scale spatial and spectral resolution remains a significant challenge.

Recently, the first label-free 3D maps of nanoscale optical modes were obtained by combining 2D electron-energy loss spectroscopy (EELS) with tomographic reconstruction methods [145, 289]. In this paper, we introduce a complementary technique for nanoscale interrogation of optical properties in three dimensions: cathodoluminescence (CL) tomography. While both EELS and CL rely on electron-beam excitation of a sample, they are fundamentally distinct in their detection mechanisms and signal interpretation. First, CL spectroscopy detects light emitted by a sample rather than the energy lost by electrons transmitted through the sample. This optical detection scheme currently allows higher spectral resolution than is afforded by EELS. Second, CL selectively detects radiative optical processes, whereas EELS indiscriminately probes both radiative and non-radiative processes. Therefore, unlike EELS, CL enables direct visualization of material luminescence and radiative decay of electromagnetic modes. Together, the high spectral resolution and selective detection of radiative processes of CL tomography could elucidate, for example, the regions of highest radiative rate enhancement near a nanostructure or the distribution of radiative recombination sites in a semiconductor.

To demonstrate this new tomographic technique, we first obtain a series of CL maps of a 3D metal-dielectric nanostructure at various orientations. Next, we use the method of filtered back projection to reconstruct the CL intensity, which
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As an example of CL spectroscopic tomography, we consider a 3D metal-dielectric crescent, or nanocup, shown schematically in Figure 8.1(a). It is composed of a sub-wavelength dielectric core coated with a tapered metallic shell. This structure is well-known for its ability to harvest light over a large bandwidth [290–292], to confine light on the nanoscale [293–297], to support electric and magnetic modes [298, 299], and to serve as the constituent of an extremely broadband negative index metamaterial at optical frequencies [300]. The plasmonic nanocrescent derives many of its interesting optical properties from the asymmetry of its core-shell geometry: the tapered metallic shell yields a broadband optical response, while the metallic discontinuity across the tips enables strong electric and magnetic resonances and field enhancements. Yet, the crescent’s rotational symmetry imparts it with a degree of insensitivity to polarization as well as relatively facile fabrication. Additionally, the complex 3D structure of the crescent provides a powerful platform for demonstrating the potential of CL tomography.

Nanocrescents are fabricated by evaporation of Au onto polystyrene spheres. Bright-field transmission electron microscopy (TEM) images of Au-polystyrene crescents are shown in Figures 8.1(b,c). The figures reveal the axial symmetry of individual crescents, as well as their high degree of uniformity.

CL spectroscopy is performed in a scanning electron microscope (SEM) [124, 183]. Figure 8.2 depicts CL measurements of crescents with different orientations, where $\theta$ is the angle between the axis of symmetry of the crescent (the $z$ axis) and the incident beam direction. Note that this coordinate system co-rotates with the crescent such that the $z$ axis is always aligned with the axis of symmetry; this axis of rotation is defined as the $y$ axis. An angle of 0° corresponds to a crescent with tips pointing toward the substrate. Figure 8.2(b) shows the result of scanning the electron beam across the center of a crescent oriented at an angle of 90°. As the electron beam passes through the tips of the crescent (darker colored lines), the CL signal peaks at a wavelength of approximately 850 nm. This lowest-energy resonance of the crescent is characterized by strong electric field enhancement near the sharp tips of the structure [293, 297], as confirmed by finite difference time domain (FDTD) simulations (see Figure 8.2(c) and Supporting Figure 8.7). The spatial and spectral characteristics of this tip mode are also well reproduced by numerical simulations of CL via the boundary element method (BEM) [301–303] (see Supporting Figure 8.12). A discussion of the factors that influence the resolution
of the CL technique, including determination of electron-sample interactions via Monte Carlo simulations, is provided along with Supporting Figure 8.13.

As the electron beam passes through the base of the crescent (lighter colored lines in Figure 8.2(b)), the CL signal exhibits a broad peak between approximately 550 nm and 700 nm. This broad feature is understood by considering three contributions: the high energy plasmonic resonance supported by the crescent, the contribution of radiation from electron-hole pair recombination in the Au shell, and luminescence from the polystyrene core of the crescent. The higher energy plasmonic modes exhibit significant field intensity near and inside the base of the crescent, as detailed in Supporting Figure 8.10. BEM CL simulations reveal, however, that radiative decay of the high energy modes alone cannot account for the strong signal at short wavelengths observed in the experiments (see Supporting Figure 8.12). By comparing CL spectra to photoluminescence (PL) spectra of both crescents and polystyrene cores, we determine that a significant portion of the CL signal at short wavelengths is due to Au [304–306] and polystyrene luminescence [307] (see Supporting Figures 8.8 and 8.9).

Before tomographic reconstruction, we probe the effect of crescent angle on CL excitation efficiency. CL line scans of various crescents at angles between 0° and 165°, in 15° increments, are collected. The normalized CL intensities at 850 nm are used to form the sinogram shown in Figure 8.2(d). From this sinogram, it is determined that the tip mode at a wavelength of 850 nm is excited for nearly all
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Figure 8.2 – Cathodoluminescence line scans (a) Schematic of the CL line scan, with the beam passing through the central z-axis of the crescent. $\theta$ is the angle between the crescent’s axis of symmetry and the electron beam. (b) Experimental CL line scan of a crescent oriented at $90^\circ$, with darker line colors corresponding to higher beam positions, as indicated in (a). (c) Cross section of the scattered electric field intensity calculated by FDTD simulations for excitation with an x-polarized plane wave propagating in the $-z$ direction at a wavelength of 874 nm, the peak in the extinction efficiency. (d) Experimental sinogram of normalized CL intensity line scans at a wavelength of 850 nm for crescents at various angles, where the vertical axis corresponds to the excitation positions shown schematically in Figure 8.2(a). As a result of the reflection symmetry of the crescent, data from $0^\circ$ to $165^\circ$ are flipped and repeated for angles of $195^\circ$ to $360^\circ$. A crescent at $180^\circ$ was not available. The dashed line overlay denotes the physical position of the center of the gap between the tips of the crescent, derived from the crescent model.

crescent angles, except for the few angles near $0^\circ$ and $180^\circ$. At these angles, the orientation of the electron beam is perpendicular to the tip gap, which results in inefficient excitation of this mode, as the electron beam preferentially couples to out-of-plane electric field components while the tip mode has a strong field oriented across the tips. A sinogram at 550 nm illustrates that CL is excited efficiently near and in the base of the crescent over a broad range of angles, as expected (see Supporting Figure 8.10).

By scanning the beam in the SEM and collecting a spectrum at each position, 2D CL maps are generated at all wavelengths concurrently. Figure 8.3 shows 2D CL
maps at a wavelength of 850 nm for crescents at different orientations with respect to the electron beam, along with schematic representations and SEM images of the crescents. Note that this series of CL maps is the 2D extension of the 1D line-scans compiled in the sinogram of Figure 8.2(d). They confirm that the various modes can be excited for a wide-range of crescent angles, and allow 2D tracking of radiative optical properties for wavelengths spanning the visible and near-infrared spectrum (see also Supporting Figure 8.11).

8.3 3D reconstruction of monochromatic cathodoluminescence

We now use tomography to map the CL signal from the crescent in three dimensions. The CL maps just discussed, as well as the TEM images, represent 2D projections of a 3D function, and as such tomography can be used to reconstruct the 3D functions. In the case of the bright field TEM image, the intensity of the
signal is related to the integrated thickness and atomic number of the constituent materials. In CL, the intensity of a given pixel in a 2D map (as in Figure 8.3) is proportional to an integral of the CL along the electron's path. In both cases, for accurate reconstruction the generated images should satisfy the projection requirement for conventional tomography, which assumes that the signal must be linear and monotonic with the property of interest.

We first reconstruct the 3D structure of the crescent from a transmission electron micrograph to assist in the interpretation of the CL tomograms. The intensity of the TEM image is related to the integrated thickness and atomic number of the constituent materials, and rigorously satisfies the projection requirement for our non-crystalline samples. We carry out the reconstruction using a crescent oriented at 90°, as in the TEM image of Figure 8.1(b). Note that with this orientation, the crescent’s axis of rotational symmetry (z) is perpendicular to the incident electron beam. Since the crescent is assumed to be rotationally symmetric, the single TEM projection of Figure 8.1(b) can be used as a virtual tilt-series spanning the full 360° of rotation [308]. To reconstruct the crescent’s structure we use the tomographic method of filtered back projection, which forms a reconstructed image by summing partial reconstructions at various angles [309–311].

Figure 8.4(a) shows the resulting TEM tomographic reconstruction. The black portions of the reconstruction correspond to regions of high atomic number, i.e. gold, whereas the dielectric core appears white, similar to the vacuum background (see also Supporting Figure 8.14). In comparing this 3D tomogram to the original TEM image in Figure 8.1(b), it is clear that reconstruction has resulted in a significantly improved spatial representation of the structure.

To reconstruct the CL signal, we consider two different tilt-series: i) a virtual tilt-series constructed from a single experimental projection utilizing the rotational symmetry of a single crescent, and ii) the experimental tilt-series of crescents described in Figures 8.2 and 8.3. We first use the 2D CL map of Figure 8.3(c)(i) as a virtual tilt-series spanning the full 360° of rotation. For this crescent oriented at 90° with respect to the electron beam (z-axis parallel to the substrate) the excited modes are identical for any angle of rotation of the crescent about the z-axis. While modes that require a z-oriented electron beam are not excited in this configuration, the trajectory dependency of the excitation of all other modes is eliminated, as they will contribute uniformly to the CL signal across all tilt angles, allowing for a scalar reconstruction. Note that this use of symmetry to simplify an otherwise complex vector tomography problem is very similar to what was done in previous EELS tomography work [289]. Furthermore, note that material luminescence is a scalar quantity and thus trajectory independent (within the small particle assumption) and thus strictly satisfies the projection requirement. In summary, we can use the individual crescent oriented at 90° for a virtual tilt-series to directly reconstruct all but the z-component of the CL signal using conventional scalar tomographic methods. Note that this method assumes negligible particle-substrate interactions, a reasonable assumption for a crescent at θ=90°, as shown by simulations provided in Supporting Figures 8.15 and 8.16.
Figure 8.4 – 3D TEM and CL reconstructions

(a) TEM tomogram based on a single projection. Panels (i–iv) correspond to different cross sections through the reconstruction, as indicated by the colored outlines. Panel (i) shows an \((x, z)\) cross-section of the reconstruction at the midpoint of the crescent, where the metal shell and the crescent geometry can be distinctly resolved. Panel (ii) shows an off-center \((x, z)\) cross-section of the reconstruction for comparison. Panel (iii) is a horizontal \((x, y)\) cross-section of the reconstruction at the \(z\) position where the crescent tips come to a point, whereas panel (iv) is a \((x, y)\) cross-section of the reconstruction at the midpoint of the crescent, clearly showing the metal shell surrounding the inner core. (b) CL tomogram at 850 nm based on a single CL map (reconstruction in \((x, y)\) planes). (c) CL tomogram at 850 nm based on experimental tilt-series consisting of 7 crescents (reconstruction in \((x, z)\) planes).

Figure 8.4(b) shows the result of a 3D tomographic reconstruction of the CL signal at a wavelength of 850 nm based on reconstructing individual \((x, y)\) planes for each value of \(z\) (for a step-by-step illustration of this technique, see Supporting Figure 8.17). As shown by these figures, the highest CL signal is localized within the gap region between the tips of the crescent panels (i) and (iii) in particular illustrate the strong field enhancements that are spatially-localized in \(z\) near the tips, as expected for this mode based on the FDTD simulations shown in Figure 8.2(c), as well as the BEM simulations provided in Supporting Figure 8.12. Significant CL intensities can also be observed near and around the metallic shell, stemming...
mostly from luminescence of the Au itself. A similarly detailed view of the CL reconstruction at a wavelength of 550 nm is provided in Supporting Figure 8.18 for comparison.

To rigorously reconstruct the complete CL signal, including modes excited in all three orthogonal directions, a fully vectorial reconstruction is needed. As no such technique exists at this time, we can approximately reconstruct the full CL signal by carefully considering a tilt-series in which the angle between the electron beam and the z-axis of the crescent is varied. The angular dependence of the excitation of the various modes strictly breaks the projection requirement, but by restricting the range of angles considered we can minimize this effect. Furthermore, we normalize the tilt-series prior to reconstruction at each wavelength to minimize the effect of the variation in excitation efficiency on the reconstruction. Although the resulting tomogram is thus not exact, it still provides useful information about the existence and qualitative 3D distribution of all excitable modes in our structure.

We consider CL maps of crescents at different orientations, some of which were shown in Figure 8.3. Note that this tilt-series is comprised of individual crescents at different orientations with respect to the fixed substrate, similar to single-particle analysis in TEM tomography [312], and thus provides information about a mean object. For this tilt-series, we obtain 2D CL maps for crescents with angles between 75° and 165°, in 15° increments (which, as a result of the reflection symmetry of the crescent, are equivalent to angles between 195° and 285°). We choose these angles because particle-substrate interactions are negligible for these crescent orientations (see Supporting Figures 8.15 and 8.16).

Reconstruction of the CL signal is then performed using the same filtered back projection method as before, except that the reconstruction is done by 2D reconstruction in the (x, z) plane for each value of \( y \). Following the example set by previous work [289], we impose the symmetry of the particle during reconstruction to enhance the quality of the tomogram. Figure 8.4(c) shows the result of the 3D reconstruction of the CL signal at a wavelength of 850 nm based on reconstructing individual (x, z) planes. This experimental multi-crescent reconstruction compares well with the reconstruction from the single projection in Figure 8.4(b), with all of the main features reproduced: the strong field enhancement near the tips in both (i) and (iii), the reduced areal cross section in (ii), and the intensity in and around the Au shell in (iv). The remarkable agreement between the two reconstruction schemes, based on two very different sets of initial data, indicates both the validity of the assumption of negligible particle-substrate interactions for the angles considered here, as well as the merits of the qualitative reconstruction scheme. The quality of the multi-crescent reconstruction is also confirmed by comparing the original CL maps to re-projections of the tomograms at the same angles as were obtained in the experiment (see Supporting Figure 8.20).
8.4 Spectroscopic cathodoluminescence tomography

Since CL is a spectroscopic technique, we can reconstruct the CL signal in three dimensions at all wavelengths in the measured 475–950 nm range. Figure 8.5 plots the reconstructed CL spectra at volumetric pixels, or voxels, along the central axis of the crescent, as indicated in Figure 8.5(a). Figures 8.5(c,d) show the associated spectra for the single- and multi-crescent reconstructions, respectively. By comparing these spectra with the colored voxels in the schematic, it is clear that the CL spectra vary significantly with position. In the metallic base of the crescent (light pink curves), the CL is strong and peaks broadly between 550 nm and 700 nm. In the dielectric between the tips of the crescent (dark curves), the CL signal peaks again, at approximately 800 nm to 850 nm. Aside from the discrepancy between the spectra in the dielectric core of the crescent (red curves), which will be discussed below, the main spectral trends are visible in both the single- and multi-crescent reconstructions.

The spatially-dependent CL can be understood by considering two factors con-
tributing to the intensity of the CL signal in this system: the radiative LDOS within the crescent structure and luminescence from Au and polystyrene. To investigate the radiative LDOS, which is a measure of the number of radiative decay pathways available to an emitter, we use a FDTD method to calculate the radiative rate enhancement, or Purcell factor (PF), at each position along the crescent axis, as shown in Figure 8.5(b). These spectra indicate that the radiative LDOS peaks in the gap region between the tips of the crescent at a wavelength of 782 nm. This calculated result is in very good agreement with the peak seen in this spatial region in the reconstructed CL spectra of Figures 8.5(c,d). Notably, the rapid fall in signal intensity for voxels farther away from the tips is remarkably similar between the calculated PF spectra and the experimental CL spectra. An alternative visualization of this data, along with individual components of the PF, are provided in Supporting Figure 8.21.

Near the metallic base of the crescent, the reconstructed CL signal exhibits a significant and broad peak between 500 nm and 700 nm, which is not fully reproduced in the calculated PF spectra. This feature is also absent from BEM CL calculations shown in Supporting Figure 8.12. Like the BEM calculations, the PF calculations do not account for material luminescence and indeed, PL measurements of individual nanocrescents reveal significant electron-hole pair recombination in the Au shell, as shown in Figure 8.5(b). The PL from the Au shell peaks at a wavelength of 593 nm, with a spectral shape that closely resembles the reconstructed CL. The narrower width of the PL spectrum may be due to the narrowband characteristic of the laser used for PL experiments, compared to the broadband nature of the electron beam as an excitation source in CL, or to the different temporal characteristics of the excitation. Also, note that the sharp feature at 568 nm is related to the dominant Raman line (-CH$_3$ symmetric stretch, 2886 cm$^{-1}$) of the PDMS substrate used in this PL experiment [313].

In the dielectric core of the crescent, the multi-crescent reconstruction reveals a peak at around 650 nm not present in the single-crescent reconstruction (compare Figures 8.5(c,d)). This peak is due to a mode that is not efficiently excited at 90°, and thus does not show up in the single-crescent reconstruction, which ignores modes that require a z-oriented electron beam for efficient excitation. This mode is identified through plane wave extinction calculations, BEM CL simulations, as well as Purcell factor calculations, which confirm the existence of a mode at approximately 600 nm excited in the center of the crescent for a z-oriented dipole, but not for x- or y- oriented dipoles (see Supporting Figures 8.7 and 8.22). The existence of this peak in the CL tomogram demonstrates the ability of the multi-crescent reconstruction to probe all modes of the system. Lastly, it is interesting to note that the spectra of both reconstruction methods show significant CL signal in the dielectric core of the crescent below 500 nm, rising up to the edge of the spectral window studied here. This signal stems from luminescence of the polystyrene bead itself [307], which peaks at approximately 450 nm (see polystyrene PL spectrum in Supporting Figure 8.9). Taken together, these results demonstrate the high spatial and spectral resolution of the experimental CL reconstructions.
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To obtain a complete sense of the spectral and spatial dependence of the CL signal, three-dimensional reconstructions at wavelengths between 470 nm and 900 nm are shown in Figure 8.6. In these images, the crescent is oriented with its tips at the top of the images. This figure contains tomograms generated from the single crescent at 90°; tomograms generated from the experimental multi-crescent tilt-series show excellent agreement and are provided in Supporting Figure 8.19. These spectroscopic CL tomograms clearly demonstrate how different spectral features contributing to the CL spectrum of a 3D nanostructure can be resolved at a spatial resolution well below the diffraction limit. Videos illustrating these reconstructions are provided online in the Supporting information of [314].

8.5 Conclusions

In conclusion, we have developed CL spectroscopic tomography as a novel technique to probe deeply subwavelength radiative optical properties in three dimensions. The technique allows spectral reconstruction of individual nanoscale volumetric pixels, spanning visible and near-infrared frequencies. The resultant tomograms reveal regions of efficient CL, with contributions from both material luminescence and radiative decay of resonant electromagnetic modes. Looking forward, we envision CL tomographic reconstructions that include momentum- and polarization-resolved information with nanometer-scale voxel resolution.
Additionally, application of CL tomography to systems beyond simple inorganic specimens should be straightforward. For example, this tomographic technique could be used to precisely locate radiative recombination centers in light emitting diodes, probe the nanoscale distribution of defect states in organic photovoltaics, and potentially provide new label-free avenues for biological imaging.

8.6 Methods

Crescent fabrication. Nanocrescents are fabricated by metal evaporation onto dielectric beads. An aqueous solution of 200 nm diameter polystyrene beads (Polysciences, Inc., coefficient of variance = 8%) is deposited onto a glass coverslip coated with polydiallyldimethylammonium chloride, a charged polymer used to improve areal coverage. The coverslip is then mounted on a rotation stage that is tilted at an angle of approximately 45 degrees and rotated at 45 rpm during the e-beam evaporation. Au is evaporated at a rate of approximately one angstrom per second until the thickness of the metal at the base of the dielectric beads reaches about 70 nm. For TEM, the crescents are removed from the substrate with a carbon grid coated with an ultra-thin layer of polydimethylsiloxane (PDMS). For CL experiments, the crescents are removed from the original substrate with a PDMS stamp and then transferred onto a clean Si wafer via a transfer printing procedure that, importantly, does not preserve their orientation. The orientation of each crescent is determined by taking SEM images at 0° and 40° stage tilt and comparing the images to a computer-generated tilt-series.

TEM imaging. TEM images were obtained using a FEI Tecnai G2 F20 X-TWIN transmission electron microscope at 200 keV in bright field imaging mode.

CL spectroscopy. CL measurements were performed in an FEI XL-30 SFEG SEM with an aluminum paraboloid mirror attached to a piezoelectric positioning system. The 30 keV electron beam passes through a 600 µm hole in the mirror directly above its focal point. The beam spot diameter was approximately 10 nm, and the typical beam current used was approximately 1 nA. The emitted radiation is collected by the mirror and directed outside the microscope into a spectrometer outfitted with a liquid-nitrogen-cooled Si CCD detector. To generate one-dimensional (1D) and 2D CL maps, the beam is incrementally scanned and a spectrum is collected at each position. For all CL experiments, the electron beam step size and corresponding pixel size, is 10 nm. The CL spectra and sinogram in Figure 8.2, which represent line scans through crescents, are smoothed by averaging the central 3 pixel lines (30 nm) of the 2D map, as well as by averaging over wavelengths in a ±5 nm range. Spectral noise in CL maps and tomograms is reduced by averaging over wavelengths in a ±5 nm range.
Numerical simulations. Plane wave and dipole excitation of the crescent are modeled using three-dimensional finite difference time domain methods, with the software FDTD Solutions by Lumerical Solutions. Electron-beam excitation is modeled using the boundary element method (BEM) [301–303]. In all cases, the simulated crescent has the following geometrical parameters: 270 nm diameter gold shell (permittivity from CRC Handbook of Chemistry and Physics); 200 nm diameter dielectric core (index = 1.47), offset in the $+z$ direction by 32.5 nm; 145 nm diameter of the tip gap; 5.5 nm radius of curvature of the tips; 1 nm mesh size. The extinction cross section under plane wave excitation is calculated as the sum of the scattering and absorption cross sections using a total-field-scattered-field source approach. The Purcell factor for a given position and orientation is calculated as the ratio of the power emitted to the far field by a dipole to the power emitted by a dipole in free space. The total Purcell factor at a given position is calculated by averaging the contributions from the three orthogonal orientations.

Tomographic reconstruction. The method of filtered back projection is used to reconstruct 3D functions from 2D projections. A ramp filter multiplied by a Hann window is used both to increase contrast and to decrease noise in the reconstructions. Complete details are provided in the Supporting information of [314].

Photoluminescence. PL spectra are collected from individual crescents on a PDMS substrate, using a focused CW Ar-ion laser operated at 488 nm. The PL spectrum shown in Figure 8.5(b) represents the average of six normalized single particle spectra. Dark-field scattering spectra are collected before and after laser illumination to guarantee that the crescents are not damaged during the experiment.

8.7 Supporting information

8.7.1 Nanocrescent mode simulations

The plasmonic modes of the crescent are determined by exciting the structure with plane waves in finite difference time domain (FDTD) simulations. The extinction efficiency, the ratio of the extinction cross section to the geometrical cross section, is calculated for various angles of incidence $\theta$, where $\theta$ is the angle between the crescent's axis of symmetry and the polarization of the electric field in the $(x,z)$ plane. The extinction spectra for angles between $0^\circ$ and $90^\circ$ in $15^\circ$ increments are shown in Supporting Figure 8.7(a).

A number of different modes can be identified from the spectra. The lowest energy mode at 874 nm, excited most efficiently at $90^\circ$, is characterized by strong
Figure 8.7 – Plane wave excitation (a) The extinction efficiency, calculated using FDTD, for plane waves at angles of incidence between 0° (light pink curve) and 90° (black curve), in 15° increments. The scattered electric field intensity at 874 nm of a crescent at 90° for cross sections of: (b) the central slice in the (x, z) plane, (c) the central slice in the (y, z) plane, (d) a slice through the tips in the (x, y) plane, and (e) a slice through the center in the (x, y) plane. The slices in (b-d) are color-coded according to the schematic in (a). Scale bar of 100 nm applies to all field maps.

The mode at 740 nm is only efficiently excited at 0°, when the electric field is oriented in the z-direction. This mode is also accessible with a z-oriented dipole or...
an electron beam propagating along \( z \), and is thus observed in the multi-crescent tomogram, as described in detail in a later section. The next section describes the highest energy mode, at 580 nm, which is most efficiently excited at 90° and is characterized by an enhanced field near the base of the crescent.

### 8.7.2 Cathodoluminescence signal at high energies

To understand the peaks in the CL spectra at high energies, we must consider not only the radiative decay of plasmonic modes, but also the luminescence from Au and polystyrene. Radiation in Au occurs when an electron in the \( d \) band is excited to an unoccupied state in the \( sp \) conduction band. Some fraction of these excited electrons recombine radiatively with the holes in the \( d \) band, resulting in emission of a visible photon. This interband transition process is typically studied by exciting the Au with light using photoluminescence (PL) spectroscopy. For smooth Au films [304], the PL quantum yield is as low as \( 10^{-10} \), and this source of radiation is thus often ignored in many CL experiments [92]. It has been shown, however, that nanoparticles of Au exhibit PL quantum yields as high as 0.04, more than eight orders of magnitude higher than Au films [305, 306, 315–318].

To demonstrate that radiation from electron-hole pair recombination in Au contributes to the CL signal of crescents, we consider both CL and PL from crescents in Supporting Figure 8.8. A TEM image of a crescent is shown in Supporting Figure 8.8(a), where, as a result of mass-thickness contrast, the intensity corresponds to the amount of Au at each location. We plot a line scan of the TEM intensity along the central axis in Supporting Figure 8.8(b), where it can be seen that the Au density peaks in the base of the crescent, as expected for this geometry.
Overlaid in the figure is a line scan of the measured CL intensity along the central axis at a wavelength of 550 nm, where Au is known to fluoresce. By comparing these two curves, we see that the CL intensity at 550 nm tracks the Au density quite well. The fact that this CL signal is correlated with the amount of Au the electron interacts with suggests that luminescence from Au contributes significantly to the CL signal at this wavelength.

To confirm this hypothesis, we measure the PL of individual crescents excited at 488 nm with a CW Ar-ion laser. An average of six single crescent PL spectra is shown in Supporting Figure 8.8(c). The sharp feature at 568 nm is a result of the dominant Raman line (-CH$_3$ symmetric stretch, 2886 cm$^{-1}$) of the polydimethylsiloxane (PDMS) substrate used in this experiment [313], which shows up as a dip in the spectrum due to imperfect background subtraction. On top of this spectrum we plot the CL spectrum at the axial position in the base of the crescent where the peak Au density is found in Supporting Figure 8.8(b), as indicated by the red dot in Supporting Figure 8.8(a). This CL spectrum is from the multi-crescent reconstruction, as explained in the text. Both the PL and the CL spectra peak near 595 nm, and exhibit similar spectral shapes. The increased breadth of the CL spectrum may be a result of the broadband nature of the electron beam as an excitation source, as compared to the extremely narrowband characteristic of the laser used for PL experiments, or due to the different temporal characteristics of the excitation.

The strong spatial agreement of Supporting Figure 8.8(b) and spectral agreement of Supporting Figure 8.8(c) suggest that radiation due to electron-hole pair recombination in Au is responsible for a significant portion of the crescent CL signal at short wavelengths.
Another source of CL at the shortest wavelengths probed in this experiment is luminescence from the polystyrene core of the crescent, as shown in Supporting Figure 8.9. A TEM image of a crescent is provided in Supporting Figure 8.9(a) for reference. Once again focusing on the central axis of the crescent, we plot a line scan of the density of polystyrene in Supporting Figure 8.9(b), calculated based on the crescent geometry used in FDTD simulations. This is compared to a line scan of the CL intensity along the central axis at a wavelength of 470 nm, at which polystyrene is known to photoluminesce [307]. While some signal at this wavelength is likely a result of Au luminescence and radiative decay of the high energy plasmonic modes, the shape of the CL spectrum suggests that a portion of the signal is originating from the dielectric core, especially in comparing Supporting Figure 8.9(b) with Supporting Figure 8.8(b).

To confirm that the 200 nm diameter polystyrene beads used as the core of the crescents exhibit PL in this spectral regime, we perform PL measurements of polystyrene beads suspended in water using a Cary Eclipse fluorescence spectrophotometer. The excitation is centered at a wavelength of 200 nm and the emission is collected after a delay of one microsecond to avoid Raman scattering. The PL spectrum, smoothed by averaging over neighboring wavelengths in a ±5 nm range, is provided in Supporting Figure 8.9(c), and is seen to peak at 450 nm, in good agreement with previous studies. Also plotted in this figure is the CL spectrum from the single-crescent reconstruction, at the axial position at the center of the polystyrene core of the crescent, as indicated by the red dot in Supporting Figure 8.9(a). In comparing these spectra, it is important to keep in mind that the luminescence of polystyrene will be modified by the presence of the Au shell. Although the PL from polystyrene beads is relatively broad, CL signal is only clearly observed within the dielectric bead in the 3D tomograms (Figure 8.6 of the main text) at the shortest wavelengths because radiation from the Au shell becomes dominant beyond 500 nm.

Of course understanding the plasmonic resonances supported by the crescent at these short wavelengths is also important when interpreting the CL signal, as radiative decay of these modes will contribute to the overall CL signal. The nature of the high energy crescent mode is elucidated by plotting the intensity of the scattered electric field at 580 nm, the peak in the extinction efficiency at high energies, when illuminated with a field polarized in the x-direction, as shown in Supporting Figure 8.10(a). It can be seen that the field enhancement is localized to the base of the crescent, both inside and outside of the metal shell. This is in contrast to the lowest energy mode at 874 nm, which exhibits the highest field intensity between the tips of the crescent. The high energy mode localized near the metallic base, while also excited directly by the electron beam, most likely enhances the radiation from Au near the base of the crescent.

The physical localization of this high energy CL signal is confirmed by examining the CL tilt series. CL line scans of crescents at angles between 0° and 165°, in 15° increments, are collected, and the normalized intensities at 550 nm are used to form the sinogram shown in Supporting Figure 8.10(b). Here, the dashed sine
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curve overlay denotes the physical position of the center of the base of the crescent, derived from the crescent model, which roughly tracks the location of the CL signal, as expected for the high energy crescent mode. The downward sloping streak of low CL intensity in the middle of the sinogram corresponds to regions where the electron passes through relatively little Au, and consequently where less Au luminescence is emitted at this wavelength. This sinogram thus suggests that the high energy CL signal is comprised of both radiative decay of the high energy crescent mode as well as radiation from electron-hole pair recombination in Au.

CL maps of crescents with different orientations help illustrate this point more completely. Supporting Figure 8.11 shows schematics, SEM images, and 2D CL maps at 550 nm for crescents at angles of 90°, 120°, and 150°, respectively. The CL maps allow us to visualize where the most efficient excitation occurs at this short wavelength. As expected, across all crescent angles, the CL signal is highest towards the base of the crescent and where the Au is thickest. Note that these maps are part of a tilt-series of 7 crescents used to reconstruct the CL signal in three dimensions via tomography.

Another way to understand the spatial and spectral dependence of crescent CL is to compare CL line scans of crescents at different angles, as provided in Supporting Figure 8.11(d) for angles of 90°, 120°, and 150°. Here, the color of the different spectra correspond to the different excitation positions indicated in Supporting Figure 8.11(a). At short wavelengths, the CL peaks consistently near the base of the crescent (light pink lines) where the high energy modes are excited and where the metal shell is at its thickest. At longer wavelengths, the peak centered in the 800–850 nm spectral range (dark brown curves) decreases in magnitude for increasing crescent angle. This is a result of reduced coupling to this mode at 180° (or 0°) when the electron beam is parallel to the crescent’s axis of symmetry. This mode is
excited at most angles, however, and the slight shift in spectral position is likely due to small differences in the geometry of the sharp tips. The excitation of this mode across nearly all crescent angles is most clearly seen in the CL sinogram at 850 nm provided in the main text, which consists of 12 different crescent angles.

8.7.3 Boundary element method simulations of cathodoluminescence

We simulate the CL experiments using the boundary element method (BEM) [301–303]. This technique models the fields generated by the swiftly moving electron and is used to simulate the coherent portion of the CL signal, including radiative decay of electromagnetic eigenmodes and transition radiation. It is important to note, however, that this technique does not reproduce the incoherent portion of the CL signal, namely material luminescence.
The crescent geometry used in the BEM simulations is the same as that used for the FDTD simulations. As a result of geometrical constraints of the code, the crescents are simulated in free space, ignoring the influence of the substrate, which should be minimal as described in a subsequent section.

Supporting Figure 8.12 shows the results of the BEM CL simulations for a crescent oriented at 90°. As a reference, Supporting Figure 8.12(a) is a color map of the experimental CL spectra for electron beam positions along the crescent’s central axis, as shown in the schematic. Supporting Figure 8.12(b) represents the same data as calculated via BEM. Note that the bright feature at long wavelengths near the tips of the crescent is present in both the experiments and the BEM CL simulations. This signal is due to the radiative decay of the plasmonic mode of the crescent, illustrated in Figure 8.2(c) in the main text, which is efficiently excited by the electron beam. On the other hand, the feature at shorter wavelengths near the base of the crescent in the CL experiments is absent in the BEM CL simulations. This discrepancy indicates that the high-energy mode illustrated in Supporting Figure 8.10(a) is not efficiently excited by the electron beam. Thus, the short wavelength CL signal at the base of the crescent in the experiments must be due primarily to material luminescence, as this type of signal is not accounted for in the BEM simulations.

The material luminescence at the base of the crescent is best understood by
considering the photoluminescence (PL) of the crescents stemming from the Au shell, as discussed above. Supporting Figure 8.12(c) shows a spatial line scan of the PL spectrum weighted by the density of Au as determined by the TEM image, to serve as a qualitative approximation of the strength of the Au luminescence as a function of beam position in the CL experiment. From this comparison, the Au PL strongly resembles the experimental CL signal at short wavelengths near the base of the crescent. Recall that the increased spectral breadth of this CL signal compared to the PL is most likely a result of the broadband nature of the electron beam as an excitation source, as compared to the extremely narrowband character of the laser used for PL experiments.

We also compare experimental 2D CL maps with maps generated with BEM. The experimental CL map at a wavelength of 850 nm for a crescent oriented at 90° is provided in Supporting Figure 8.12(d). Supporting Figure 8.12(e) shows the BEM CL map at 775 nm, the peak wavelength in the simulations. These maps illustrate the excellent agreement between experiment and theory for the plasmonic tip mode. The weak signal in the metal shell in the experimental map is due to material luminescence, which is not accounted for in the simulations.

8.7.4 Electron-sample interaction simulations

Many factors influence the physical limits of resolution of the CL tomography technique. Most importantly, the lateral resolution of CL imaging is limited by the spot size of the electron beam and the radial extent of the evanescent field associated with the swiftly moving electron. Using an accelerating voltage of 30 kV and a beam spot diameter of approximately 10 nm, as in our case, previous work has found a lateral resolution of 30-40 nm [124].

The resolution in the third dimension will depend on the complex interactions of the electrons with the sample, and is thus highly dependent on the particular sample. To estimate the effect of electron-sample interactions on resolution for the crescents studied here, we have simulated electron trajectories using three-dimensional Monte Carlo software [122]. As a result of constraints of the simulation software, a simplified crescent-like object is considered. The crescent consists of a 270 nm diameter Au sphere with a 200 nm diameter polystyrene sphere enclosed within it. The center of the polystyrene sphere is displaced by 69 nm with respect to the center of the Au sphere, such that the Au shell has a thickness of 1 nm at its thinnest point, which corresponds to the center of the tip gap in the real crescent. A beam diameter of 1 nm is considered.

By tracking the trajectories of 10,000 electrons as they pass through the crescent in a particular orientation, we are able to statistically determine the divergence of the beam. Supporting Figure 8.13 depicts the electron-sample interactions for two representative crescent orientations. This figure indicates that for a 30 keV electron beam, 50% of the electrons deviate from their original path by less than 25 or 80 nm after passing through the entire structure, for vertically or horizontally oriented crescents, respectively. In other words, the beam width averaged over the
Figure 8.13 – Estimating electron trajectories Statistical analysis of Monte Carlo simulations reveal the divergence of electrons as a function of depth as the 30 keV beam passes through the crescent. A cumulative probability of 0.5 at a divergence of 25 nm indicates that 50% of the electrons have deviated by less than 25 nm at the given depth. A horizontally oriented crescent (a) and a vertically oriented crescent (b) are considered.

entire thickness of the crescent is between 12 and 70 nm. This unavoidable beam divergence will influence the effective lateral resolution of a 2D CL image, and thus the resolution of the 3D tomograms as well. We note, however, that the 2D CL map calculated with BEM in Supporting Figure 8.12, which assumes zero beam divergence, matches the experimental map quite well. Furthermore, the CL voxel spectra in Figures 8.5(c,d) in the main text correspond very well with the local density of optical states (Figure 8.5(b)) calculated for discrete points using FDTD. Generally, the agreement between experiments and theory indicate that beam divergence is not a significant issue for CL tomography of the metal-dielectric crescent. It is worth noting that the divergence of the beam is reduced by an order of magnitude for 300 keV electrons, such as can be obtained in a TEM.

8.7.5 Reconstructed crescent geometry

To define the crescent geometry for modeling purposes, we more closely investigate the geometry of the TEM reconstruction. Based on the reconstruction, we choose the model crescent to consist of a 200 nm diameter dielectric core and a 270 nm diameter Au shell displaced by 32.5 nm. The gap in the tips is chosen to be 145 nm, resulting in tips with a radius of curvature of 5.5 nm. A side-by-side comparison of the central slice of the reconstruction to the central slice of the model is provided in Supporting Figure 8.14. Visual inspection suggests that the simulated geometry (red) is quite similar to the TEM reconstruction (black), aside from the detailed geometry of the tips, which are sharper in the experiment.

To quantitatively compare the two geometries, we project the density of each along two orthogonal axes. The plot at the top of Supporting Figure 8.14 depicts
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Figure 8.14 – Reconstructed crescent geometry Central slice of the TEM reconstruction (black) and the model used in FDTD (red). Projected densities along the vertical (top) and horizontal (right) directions show excellent agreement between the two geometries.

the projection in the vertical direction, while the plot at the right of the figure depicts the projection in the horizontal direction. These projected densities illustrate the excellent agreement between the model geometry and the experimental TEM reconstruction.

8.7.6 Effect of substrate on crescent tilt-series

To construct a tilt-series of crescents for tomographic reconstruction, we must rely on distinct crescents with different orientations relative to the substrate. This is due to the inability to tilt the sample in the CL SEM. An important assumption of this multi-particle tomography method is that the properties under study are not significantly affected by the substrate. We justify this assumption by considering two important dipole locations, as shown in Supporting Figures 8.16 and 8.15.

The first dipole is located in the metal base of the crescent, 55 nm from the outer edge, as depicted in the schematic inset of Supporting Figure 8.15(a). This dipole location is chosen because of the importance of metal luminescence in the CL signal. The second dipole is located in the dielectric core of the crescent, 72.5 nm from the outer edge along the crescent’s axis of symmetry, and oriented perpendicular to the substrate (refractive index = 3.7), as depicted in the schematic inset of Supporting Figure 8.16(a). This dipole location is chosen for its ability to excite both the low energy gap mode at the tips of the crescent, as well as higher energy modes. The angle between the crescent’s axis of symmetry and the substrate normal is defined...
Figure 8.15 – Substrate effects The Purcell factor (PF), or radiative rate enhancement, for a dipole located inside the metal base of the crescent. The angle between the crescent’s axis of symmetry and the substrate normal is defined as $\theta$, as shown in the schematic inset. (a–i) Data for angles of 0°, 30°, 60°, 75°, 90°, 105°, 120°, 150°, and 180° are shown. The PF with no substrate (black curves) are compared to the PF with substrate (refractive index n=3.7) for each angle $\theta$ (red curves).

as $\theta$. Note that in the absence of particle-substrate interactions, angles of $\theta$ and $180^\circ - \theta$ would give the same response.

Supporting Figures 8.15(a–i) and 8.16(a–i) (red curves) plot the Purcell factor, or radiative rate enhancement, spectra for angles of 0°, 30°, 60°, 75°, 90°, 105°, 120°, 150°, and 180°, respectively. The black curves represent the PF when no substrate is present. Supporting Figure 8.15 demonstrates that the substrate has a negligible effect on the LDOS within the base of the metal shell of the crescent. From Supporting Figure 8.16, it can be seen that the substrate diminishes the intensity of the peak near 800 nm for angles close to 0°. For angles of 75° and above, however, the effect of the substrate is minimal, as the spectra with and without substrate agree well. For these reasons, we perform the multi-crescent tomographic reconstruction using a tilt-series composed of crescents at angles of 75° and above.
Figure 8.16 – Substrate effects The Purcell factor (PF), or radiative rate enhancement, for a dipole located inside the crescent’s dielectric core. The angle between the crescent’s axis of symmetry and the substrate normal is defined as θ, as shown in the schematic inset. (a–i) Data for angles of 0°, 30°, 60°, 75°, 90°, 105°, 120°, 150°, and 180° are shown. The PF with no substrate (black curves) are compared to the PF with substrate (refractive index n=3.7) for each angle θ (red curves).

8.7.7 Step-by-step cathodoluminescence reconstruction

To elucidate the reconstruction of the CL signal by the method of filtered back projection, we illustrate the step-by-step process in Supporting Figure 8.17. For simplicity, we explain the reconstruction based on a single CL image, but the method is general and is used for the reconstruction based on the full tilt-series, as well. Supporting Figure 8.17(a) shows the CL map at 850 nm for the crescent oriented at 90°, with its axis of rotational symmetry perpendicular to the incident electron beam. Assuming the crescent is rotationally symmetric and ignoring any substrate effects, we can use this CL map as a virtual tilt-series spanning the full 360° of rotation.

As mentioned before, the 3D reconstruction is accomplished by carrying out a 2D reconstruction in the (x, y) plane at each value of z. For this example, an intermediate value of z is chosen, as highlighted by the blue box in Supporting Figure 8.17(a). This data is a CL line scan through the crescent, perpendicular to its axis of symmetry, as shown by the black curve in Supporting Figure 8.17(b), where
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Figure 8.17 – CL reconstruction method (a) 2D CL map at 850 nm of the crescent at 90°. The blue box encloses the z height used in the reconstruction. (b) CL line scan before (black) and after (red) filtering in the frequency domain. (c–f) Reconstructions in the (x, y) plane made with the method of back projection using 1, 2, 4, and 360 angles, respectively.

data points beyond the boundaries of the scan have been set to zero. The red curve in this plot is the CL signal after being filtered in the frequency domain by a ramp filter multiplied by a Hann window (See Supporting information of [314]).

To illustrate the back projection method, reconstructions using an increasing number of angles are provided in Supporting Figures 8.17(c–f). When only a single angle, 0°, is used for the reconstruction (Supporting Figure 8.17(c)), it can be seen that the filtered function is simply smeared across the reconstructed image plane in the vertical direction. When two angles, 0° and 90°, are used (Supporting Figure 8.17(d)), the vertical and horizontal back projections sum to give a square-like pattern. With the four angles 0°, 45°, 90° and 135° (Supporting Figure 8.17(e)), the donut-like form begins to take shape. Supporting Figure 8.17(f) shows the complete reconstruction using 360 angles, or a projection every degree. From these figures it is clear that the accuracy of the reconstruction is dramatically improved through the use of projections at multiple angles. It is also important to note, however, that even with only 4 angles, the general shape of the reconstructed function is apparent. This indicates that the tomogram based on the actual tilt-series data, which makes use of 14 angles, should, in fact, capture the essence of the 3D CL signal.
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Figure 8.18 – 3D TEM and CL reconstructions at 550 nm (a) TEM tomogram as a visual aid for comparing structure to CL intensity. Panels (i–iv) correspond to different cross sections through the reconstruction, as indicated by the colored outlines. (b) CL tomogram at 550 nm based on a single CL map (reconstruction in (x,y) planes). (c) CL tomogram at 550 nm based on experimental tilt-series consisting of 7 crescents (reconstruction in (x,z) planes).

8.7.8 Cathodoluminescence tomogram at high energy

As mentioned, the tomographic reconstruction of the CL signal is performed at each wavelength. Supporting Figure 8.18 shows the CL tomogram at a wavelength of 550 nm. Supporting Figure 8.18(b) is a tomogram based on a virtual tilt-series, while Supporting Figure 8.18(c) is a tomogram based on an experimental tilt-series, as described in the text and elaborated in the next section. At this wavelength, the CL intensity is primarily localized to the regions of the crescent containing Au (indicated by the black portions of Supporting Figure 8.18(a), a TEM tomogram). This corroborates the assertion that the CL signal at shorter wavelengths is primarily a result of luminescence from the Au shell.
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Figure 8.19 – 3D CL Spectroscopic Tomography
Reconstructed CL signal based on experimental tilt-series (reconstruction in \((x,z)\) planes) at wavelengths of (a) 470 nm, (b) 550 nm, (c) 650 nm, (d) 700 nm, (e) 750 nm, (f) 800 nm, (g) 850 nm, and (h) 900 nm. The reconstructed intensity corresponds to both the color scale and the transparency of the figure.

8.7.9 Cathodoluminescence tilt-series reconstruction and reprojection

As described in the text, while the rotational symmetry of the crescent allows for a simple reconstruction of the CL signal from a single CL map, this symmetry is not a requirement of the CL tomography method. We also reconstruct the CL signal with the CL maps of crescents at different orientations. For this tilt-series, we consider crescents with angles between 75° and 165°, in 15° increments, ignoring angles between 0° and 60° for the reasons stated above. As a result of the reflection symmetry of the crescent, crescents at angles between 75° and 165° are equivalent to those at angles between 195° to 285°, and thus the tilt series is composed of 14 different angles. To reduce the effect of the angular dependence of the excitation of the various modes, we normalize the intensities of the 2D maps in the tilt-series at each wavelength prior to reconstruction. Thus, although the angular dependence strictly breaks the projection requirement, we minimize the effect and the resulting qualitative reconstruction still provides useful information about the existence and 3D distribution of all excitable modes in our structure. Finally, following the example set by prior work [289], we impose the particles’ rotational symmetry during the reconstruction process to enhance the tomograms.

Supporting Figure 8.19 shows the 3D CL tomograms at wavelengths between 470 nm and 950 nm. In these figures, the intensity of the reconstructed function
corresponds to both the color scale and the transparency of the figure. These CL tomograms agree remarkably well with the CL tomograms shown in the main text, generated from the single crescent virtual tilt series. Most importantly, for shorter wavelengths we see that the CL signal is concentrated primarily in the metallic shell of the crescent, as expected for radiation from the Au. At longer wavelengths, efficient excitation of the gap mode can be seen clearly towards the top of the tomograms, near the tips of the crescent, as predicted by theory.

To confirm the quality of this multi-crescent reconstruction, we re-project the reconstructed volumes at the same angles as were obtained in the experiment. These reprojections, along with the original 2D CL maps of crescents at various angles, are provided in Supporting Figure 8.20. The excellent agreement between the original maps and the reprojections across all wavelengths and angles is indicative of the high fidelity of the multi-crescent reconstruction. This comparison is also useful in demonstrating the validity of generating a tomogram from many different nearly identical particles. Recall that the tomograms and thus the reprojections are based on 7 different crescents at 14 different angles. The strong agreement between these reprojections and the 2D CL maps of individual crescents is an indication of the similarity between the particles as well as the validity of the assumptions made.
8.7.10 Purcell factor calculations

A comparison of the single- and multi-crescent reconstructions to Purcell factor (PF) calculations was provided in Figure 8.5 of the main text. A more detailed analysis is provided in Supporting Figure 8.21. Reconstructed CL spectra at voxels along the central axis of the crescent for the single- and multi-crescent reconstructions are shown in Supporting Figures 8.21(b,c). The spectral color maps show excellent agreement for the plasmonic tip mode at wavelengths around 850 nm, as well as for the material luminescence in the base of the crescent at shorter wavelengths. In the dielectric core of the crescent, however, the multi-crescent reconstruction reveals a peak at around 650 nm not present in the single-crescent reconstruction.

To identify this feature, we calculate the Purcell factor (PF) within the crescent. The average PF is shown in Supporting Figure 8.21(d). By comparing the PF for x- or y-oriented dipoles in Supporting Figure 8.21(e) with the PF for a z-oriented dipole in Supporting Figure 8.21(f), we determine that the peak in the center of the dielectric core in the multi-crescent reconstruction is due to a mode that is not efficiently excited at 90°, and thus does not show up in the single-crescent reconstruction, which ignores modes that require a z-oriented electron beam for efficient excitation. Recall that this mode is also excited by a plane wave, but only when the electric field is oriented in the z direction.
Figure 8.22 – Identification of the mode in the center of the crescent. Spectral comparison of the BEM CL intensity at the center of a crescent oriented at 0° (blue line), the $z$-component of the Purcell factor ($PF_z$) at the center of the dielectric core (green line), and the experimental CL intensity at the center of the dielectric core from the multi-crescent reconstruction (red line).

Additional insight into this feature is provided by BEM CL simulations of a crescent oriented at 0° (with the crescent’s axis of symmetry parallel to the electron beam). Supporting Figure 8.22 shows a spectrum of the BEM CL intensity for an electron beam at the center of the crescent, along with the experimental CL intensity at the center of the dielectric core from the multi-crescent reconstruction. For comparison, the figure also includes the $z$-component of the PF at the same position. Note that the blue-shift of the simulated spectra with respect to the experimental spectrum is likely due to the substrate, which is not considered in the simulations. The agreement between these three spectra confirms that the peak at the center of the core of the crescent is, in fact, a mode that requires a $z$-oriented source for efficient excitation. This comparison also demonstrates the ability of the multi-crescent reconstruction to probe all modes of the system.