Direct imaging of hybridized eigenmodes in coupled silicon nanoparticles: supplementary material

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1. SAMPLE FABRICATION

12 × 12 mm pieces of silicon-on-insulator (SOI) wafer (100 nm Si layer, 300 nm SiO₂ layer) were first cleaned by 10 min of sonification in acetone, 5 min of sonification in isopropanol (IPA), and blow dried. After a bake-out at 110°C, the samples were cooled with N₂ and spin coated with hydrogen silsesquioxane (HSQ, Fox 15), diluted with methylisobutylketone (MIBK) in a 1:2 ratio (3000 rpm, 45 s). The resist was baked at 180°C for 2 min, after which a small droplet of water containing 50 nm diameter Au colloids was deposited in the corner of the sample, to allow for accurate alignment of the electron microscope.

Electron beam lithography is performed using a Raith e-LINE system. Single squares and dimers were written in the HSQ resist using area exposure (30 kV acceleration voltage, 7.5 μm aperture, 17.8 pA beam current) and a dose of 1150 μAs/cm². The resist was developed by submerging in MF-319 (Microposit developer) at 50°C for 70 s, and subsequently rinsed in deionized water to stop the development.

Next, the HSQ pattern was used as an etch mask during the reactive-ion etching (RIE) step. An Oxford PlasmaPro 100 Cobra was used to anisotropically etch away the Si top layer. First, a short (10 s) Cl₂-based etch (50 sccm Cl₂, 7 mTorr, 30 W forward power, 750 W ICP power) was used to etch away the native oxide formed on the sample. Next, a 40 s etch using HBr (48 sccm) and O₂ (2 sccm) was used to anisotropically etch through the Si layer (7 mTorr, 30 W forward power, 750 W ICP power). The substrate temperature was controlled at 50°C during the etching. Finally, the residual HSQ etch mask was removed by a 2 min dip in hydrofluoric (HF) acid (1% concentration in water), and subsequently rinsed in deionized water and blow dried.

2. DARK-FIELD SPECTROSCOPY

Dark-field scattering spectra of the single particles and dimers were obtained using a WiTec α300SR microscope. The sample was illuminated (unpolarized dark field configuration) using a 100× Zeiss microscope objective (EC Epiplan-Neofluar, HD M27, 0.9 NA, 0.28 mm working distance) and a halogen lamp. Scattered light was focused into a 50 μm-core collection fiber and sent to a spectrograph (UHTS 300, WiTec, 600 lines/mm, center wavelength 500 nm), equipped with a back-illuminated CCD camera (1024 × 127 pixels, *T* = −60°C). The experimental spectral range was 430–570 nm.

During the experiment, the sample was scanned through the focus of the objective in a two-dimensional plane using a 3D-piezo stage. Each scan used 15 × 15 pixels over a scan area of 3 × 3 μm (200 nm step size), with a 1 s integration time per pixel. Figure S1 shows a typical intensity map obtained from the scattering of a single particle ($\lambda = 472$ nm). Data is averaged over the pixels that have an intensity larger than 85% of the maximum observed intensity (threshold) to increase the signal to noise (e.g. 3 pixels in Fig. S1). To correct for the system response, a Lambertian reference was used (Labsphere certified reflectance standard). The dark-field scattering spectra are calculated as $(I_{part} - I_{dark}) / (I_{lamb} - I_{dark})$, where I_{part} is the scattering spectrum of the particle, I_{lamb} the lambertian reference spectrum, and I_{dark} the dark spectrum of the CCD.

Note that the particle spacings reported in Fig. 2 in the main text are obtained from SEM images, using a thresholding routine and the calibrated pixel size.

Fig. S1. Intensity map of a typical dark-field measurement. Map is for a single particle at $\lambda = 472$ nm.

3. CATHODOLUMINESCENCE SPECTROSCOPY

A scanning-electron microscope (FEI XL-30 SFEG) was used to irradiate the nanoparticles with a focused electron beam (30 keV, ~ 20 nA current). The CL radiation is collected by an Al parabolic mirror and redirected out of the SEM. Spectral analysis was performed using a spectrograph (Acton SpectraPro 2300, 150 lines/mm, center wavelength 650 nm) and a liquid-nitrogen cooled back-illuminated CCD camera (Spec 10 100B, Princeton instruments, 1340×100 pixels). The CCD chip was hardware-binned to 335×1 pixels. During the scans, the electron beam was scanned over the particle using a 50 ms integration time per pixel. The CL data are corrected for system response using a measured transition radiation spectrum from aluminium and comparing that to theory [1, 2]. The background CL signal from the substrate was subtracted from the measured data, which includes the transition radiation of the SiO_2 layer and Si substrate, as well as intrinsic defect luminescence from the SiO_2 . To correctly subtract the variable background from the CL signal, we use a triangular interpolation routine, which interpolates the background intensity between the corners of the scan for each wavelength. We used thresholding of SEM data to determine which pixels contribute to the particle CL spectra.

4. EIGENMODE CALCULATIONS

Finite-element modeling was performed using COMSOL Multiphysics 5.0. The simulation volume was a quadrant of a sphere, with a radius of 480 nm, and was surrounded by a PML layer with 240 nm thickness. The dimers were positioned in the center of the sphere. The simulation volume used a homogeneous relative permittivity of 1, while a non-dispersive relative permittivity of 20 was used for the silicon particles. For the flat sides of the quarter sphere we used perfect electric or magnetic conductor boundary conditions, depending on the orientation and nature (electric or magnetic) of the dipole resonance. In the simulation volume mesh elements were tetrahedral, with vertex lengths between 0.3–10 nm inside and close to the silicon particles and 30 nm near the PML boundary. The PML mesh was swept from the PML boundary, with five layers along the radial direction and a maximum transverse vertex length of 30 nm.

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