Dark plasmonic breathing modes in silver nanodisks - Supporting Information

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EEL map acquisition (experiment)

The experimental EEL maps shown in Figure 1b of the main part were acquired with the STEM-EELS technique (STEM scanning transmission electron microscope, EELS electron energy loss spectroscopy), scanning a 200 keV electron beam over the region of interest and taking EEL spectra with an energy-resolution of 0.12 eV at each pixel (Supporting Figure 1). Due to stable experimental conditions during the measurement we used an exposure time per pixel of 0.2 seconds. To account for the lower signal of elastically scattered electrons when the electron beam transits the silver disk (position 1 in Supporting Figure 2a) as compared to trajectories through the silicon nitride substrate only (position 2 in Supporting Figure 2a), spectra were normalized to their according zero-loss intensity (inset in Supporting Figure 2). As illustrated in Supporting Figure 2b, the breathing mode peak around 2.5 eV (position 1) without normalization is of comparable intensity as the tail of zero loss peak measured on the substrate (position 2). Only by normalizing,

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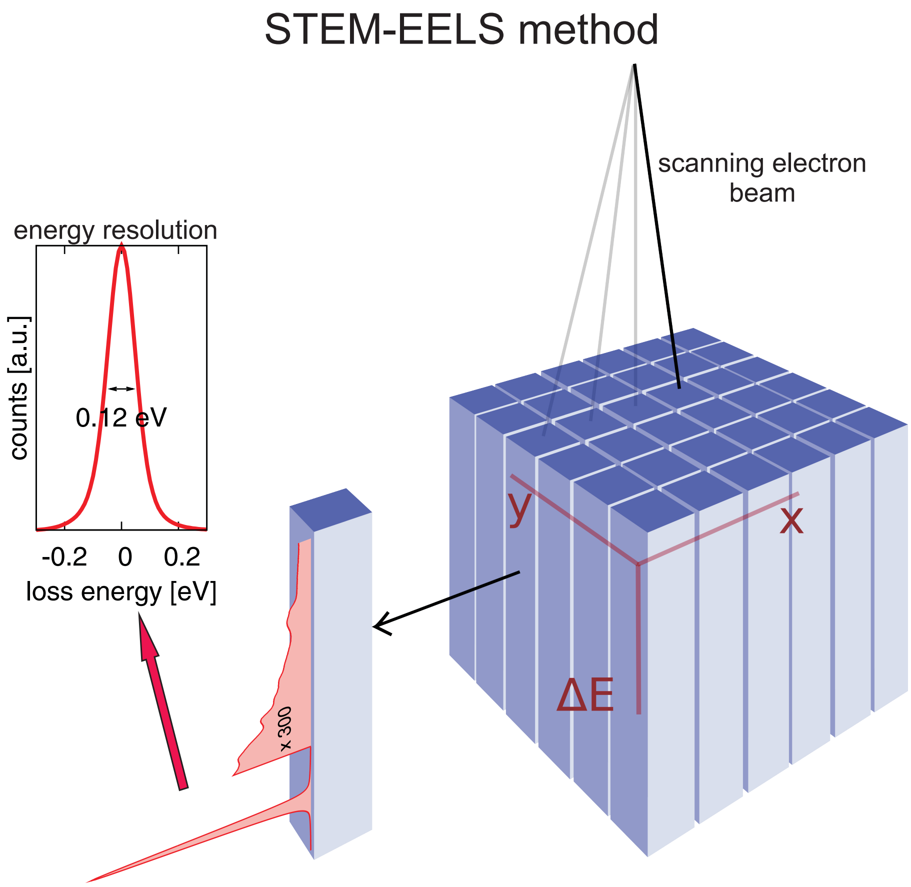
the correct relative signal strengths are recovered. In addition, the zero-loss signal was subtracted from each individual spectrum using a fitted logarithmic function ("fitted logarithm tail" model within Digital Micrograph software [Gatan, USA]). All EEL maps in Figure 1b were measured on the same silver nanodisk of 200 nm in diameter, while the single spectra in Figure 2a were acquired in the middle of nanodisks with diameters ranging from 130 to 1000 nm. The single spectra were also zero-loss subtracted using the same subtraction procedure as mentioned above and smoothed by averaging EEL-counts over an energy-width of 0.1 eV.

Surface charge distribution (simulation)

To simulate EEL maps of the silver nanodisk in Figure 1 in the main part and to calculate surface charge distributions on this particle as a function of loss energy and position, the MNPBEP matlab toolbox was used (see Ref. 21 in main article). For the computation of surface charge distributions, the electron beam was set to 3 different positions on the silver particle (in the center, at half radial distance (R/2) and on the edge), while the energy loss was varied for each position between 2 to 4 eV (center position) and 1 to 4 eV (R/2 and edge) with an energy step size of 0.01 eV. Surface charge maps as a function of loss energy are summarized in three Supporting Videos. Video 1 shows the spectral evolution of the surface charge distribution for the center position of the electron beam, while Video 2 and 3 refer to the R/2 and edge positions, respectively.

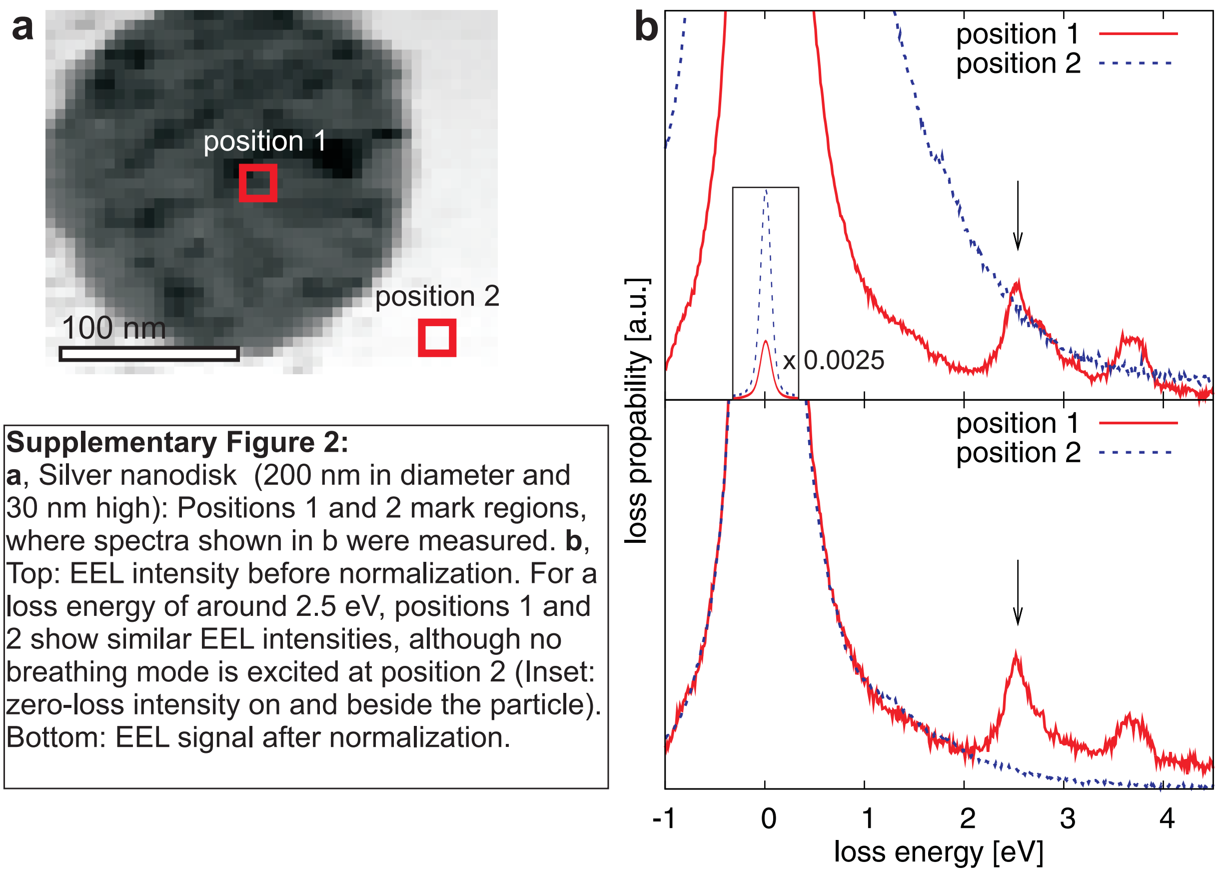
Numercial calculation of the surface plasmon dispersion relation

For calculating the surface plasmon dispersion we applied the optical transfer matrix method which allows to calculate the amplitudes of the plane waves reflected and transmitted by a multilayer system in relation to an incoming plane wave. As surface plasmons are bound modes the incoming wave is assumed evanescent, akin of the Otto excitation scheme but with the coupling prism considered at infinite distance. To obtain the dispersion of the plasmon mode of the vacuum-Ag-silicon nitride-vacuum system with a field maximum at the silver-silicon nitride interface, the exciting evanescent wave was assumed to be incident from the vacuum-side of the silver film. For a given wavenumber, the frequency was varied to find the (local) maximum amplitude of the transmitted (evanescent) wave, which indicates the optimum condition for exciting this surface plasmon mode with real wavenumber (i.e., no spatial decay) and real frequency (no temporal decay). This leads to the dispersion relation, which is probed by the experiments where the wavenumber of the breathing mode is defined by the disk diameter and the frequency of maximum excitation probability is selected from the EEL spectra.



Supplementary Figure 1:
Schematic view of the used measurement technique (STEM-EELS): At every image position (x, y) an EEL spectrum is recorded. By plotting the EEL intensity at a given energy vs. the coordinates (x, y), EEL maps ("spectral images") as presented in figure 1 are derived from these data. Inset: Zero-loss peak with an energy width of 0.12 eV (FWHM).

Normalization process



Supplementary Figure 2:
a, Silver nanodisk (200 nm in diameter and 30 nm high): Positions 1 and 2 mark regions, where spectra shown in b were measured. **b**, Top: EEL intensity before normalization. For a loss energy of around 2.5 eV, positions 1 and 2 show similar EEL intensities, although no breathing mode is excited at position 2 (Inset: zero-loss intensity on and beside the particle). Bottom: EEL signal after normalization.