Supporting Information

Direct Observation of Plasmon Band Formation and Delocalization in Quasi-Infinite Nanoparticle Chains

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Keywords:
surface plasmons, nanoparticle, template-assisted self-assembly, electron-energy loss spectroscopy
Figure S1: **Infinite chain limit by plane wave excitation.** By steadily increasing the chain lengths the excitation wavelengths shift to longer wavelengths, i.e., lower energies. As shown in the inset, the longitudinal L1 mode converges to certain energy. In literature, this typically defines the infinite chain limit and is reached at about $10^{-12}$ particles.\(^\text{1,2}\) Whereas at 20, the L3 superimposes with the L1 and becomes negligible. Thus, in the infinite chain limit, the assembly sustains a band of plasmon modes.

Figure S2: **EELS probability map of an isolated gold nanoparticle.** The single particle exhibits a basic LSPR mode at 2.25 eV, which identifies as transversal mode for particle chains (>1 particle), as shown in the main text.

Figure S3: **Example illustrating the treatment of low-loss EELS spectra.** The row spectra (filled) is aligned to zero energy by the Non-Linear Least Square (NLLS) fitting. The reference profile of a zero-loss peak (green curve) is deduced by averaging about thousand spectra collected far away from the gold particles, i.e. consisting of no plasmon excitations. Each individual spectrum was aligned to zero energy by the NLLS fitting before averaging. Then, the reference profile is normalized to the intensity of the row spectra and subtracted from the latter resulting in the plasmon excitation spectrum (red curve). Note that plasmon peaks are typically of 3 orders of magnitude weaker than the zero-loss peak, thus the subtraction might be inaccurate in the vicinity of the zero energy where the tiny differences in the peak profile and its exact energy position are visible. In the present work, we discarded the energy range below 1 eV.
Figure S4: Examples of low-loss EELS spectra from spectrum-imaging of chains with a different number of gold nanoparticles. The number of particles in the chain is displayed on top of each spectrum. Filled profiles show the spectra averaged over the whole area of spectrum-images while green, blue and red curves show examples of the spectra picked from the selected parts of spectrum-images (averaged over the area of 10–40 pixels). Arrows denote the central positions of the different peaks eventually recognized in spectra.
**Figure S5: Particle chains close to and beyond the infinite chain limit:** Schemes, simulated surface charge plots of the L* mode, and electron energy loss mappings for all selected plasmonic modes (a–b; 10 and 15 particles, respectively; experimental left and simulated right) For 10 particles (a), the L2 and L1 mode start to merge in both the simulation and the experiment, whereas the L3 is still isolated observable – marking thereby the transition from plasmonic oligomer to polymer.
Figure S6: Simulated surface charge plots of the lowest-order mode (L1 or L*, respectively) for direct comparison. By increasing the chain length, at roughly 10 particles a pinch-off of the induced dipole moment in the center can be observed, which indicates the superposition of the L1 and L3 mode and the formation of the plasmon band (≥10 particles, as indicated by the dotted box).
Figure S7: Simulated EELS spectra from 1 to 30 particles. The exciting electron beam was placed 50 nm from the terminal gold particle in longitudinal direction. Due to increasing damping of gold towards lower energies, the L1 mode becomes indistinguishable above 8 particles (where it appears as a small shoulder at 1.4 eV). Beyond 10 particles higher order Lm modes superimpose, thereby forming the L* mode.

For the transversal mode, the calculations predict a minor shift of 0.04 eV to higher energies due to its anti-bonding character. The respective bonding mode is dark and consequently not observed. The shift is, however, not detected in experiments because it is far below the measurement accuracy. Consequently, the transversal mode consists of only weakly coupled individual particle modes. In contrast, both experiments and simulations suggest that the energies of all longitudinal modes decrease with increasing the number of particles in a chain.
Figure S8: Plasmonic polymer spectrum (FDTD simulation) excited by a dipole source. In order to probe the energetic position of waveguiding modes in a particle chain consisting of 20 particles a broadband dipole source was placed at the end of the chain and the extinction, absorption, and scattering coefficient was computed (a). The dashed lines highlight the spectral position of the modes (picked according to the absorption peak positions), which are used for the waveguiding simulations in the main text. The role of the overlapping modes is visualized by multipeak-fitting of the extinction spectrum (b). The efficient waveguiding modes feature a significant overlap with the neighboring modes, thereby forming the energy band.
Section S1: Discrete Dipole Model

In the following some more details of the discrete dipole model are provided including explicit expressions for the propagators and derivations of the main results noted in the main text. The propagator for the dipole radiation including retardation effects reads

\[ G_{ij}(\omega) = \frac{e^{ikr_{ij}}}{4\pi\varepsilon_0} \left\{ \frac{k^2}{r_{ij}} (1 - \hat{r}_{ij} \otimes \hat{r}_{ij}) + (1 - ikr_{ij}) \frac{3\hat{r}_{ij} \otimes \hat{r}_{ij} - 1}{r_{ij}^3} \right\}. \]

The corresponding expression \( G_{ij,\text{ref}}(\omega) \) for the reflected fields is noted in the book of Novotny and Hecht (cf. Eq. 10.16).\(^4\) Restricting the discrete dipole model do nearest neighbor interactions, taking into account the dominating diagonal coupling only, and linearizing the polarization within the frequency regime considered

\[
\left( \alpha_0^{-1} + a\omega + \sum_{j=i\pm 1} G_{xx}(\omega) \right) P_{x,i}(\omega) = E_{x,\text{ext}}(\omega)
\]

permits to find the longitudinal modes as the eigenvectors of the following \( n \times n \) (with \( n \) being the number of nanoparticles) coupling matrix (here the constant \( a \) is absorbed into the \( G_{xx} \) and \( \alpha_0^{-1} \))

\[
\begin{pmatrix}
\alpha_0^{-1} & G_{xx} & \cdots & 0 \\
G_{xx} & \alpha_0^{-1} & \ddots & \vdots \\
\vdots & \ddots & \ddots & G_{xx} \\
0 & \cdots & G_{xx} & \alpha_0^{-1}
\end{pmatrix}
\]

This matrix has tridiagonal Toeplitz structure with \( n \) eigenvalues

\[ \omega_t = \omega_0 - 2G_{xx} \cos \frac{l\pi}{n+1}, l \in \{1, \ldots, n\} \]

and corresponding eigenvectors (particle index vector \( j \))

\[ P_i = \sin \frac{j l\pi}{n+1}, l \in \{1, \ldots, n\} \]

denoted by \( j \). In the infinite chain limit \( n \gg 1 \) \((L = nd)\), the analytic dispersion relation reads \( \omega(q = \pi l/L) = \omega_0 - 2G_{xx} \cos(qd) \). Thus, a band of eigenvalues with \( \omega_{\text{min}} = \omega_0 - 2G_{xx} \) emerges, whose width may be controlled by the dipole coupling strength (\( e.g., \) particle distance). Finally, the optical coupling strength per mode is given by the analytical expressions for the net dipole moment

\[ P(q) = \sum_j P_j(q) \approx \frac{1}{d} \int_0^L \sin(qx) dx = \frac{1}{qd} (1 - \cos(qL)) \]

of the \( q \)-dependent modes (\( e.g., \) optically dark modes have a net dipole moment of zero). Accordingly, dark modes appear, whenever \( q = \frac{2m\pi}{L} \) and the largest net dipole moment is realized in the long wavelength limit \( q \to 0 \) (bright and dark modes highlighted in red and blue in Figure 6a in the main text, respectively). In combination with the analytical expression for density of states (DOS) of 1D longitudinal states in the infinite chain limit

\[ \text{DOS}(\omega) = 2 \frac{dq(\omega)}{d\omega} = \frac{1}{G_{xx} \Delta x} \frac{1}{\sqrt{1 - \left( \frac{\omega_t - \omega}{2G_{xx}} \right)^2}}, \]

which also grows toward the minimal excitation energy, we may conclude that the integrated optical coupling proportional to the product \( P \times \text{DOS} \) is maximal at the lower edge of the band, which is readily observed in the numerical calculations (Figure S1).
We finally sketch the derivation of the general expression for discrete dipole model of on infinite periodic lattices. To this end we write the position vector of the NPs $\mathbf{r}_i = \mathbf{r}_a + \mathbf{r}_n$ as a superposition of a basis vector within the unit cell (index $a$) and the unit cell position (index $n$). Using this convention, the dipole propagator reads $G_{\mu\nu}(r_i - r_j, \omega) = G_{a\mu}^{by}(n - n', \omega)$. The discrete dipole model (Eq. 1 in main text) can now be partly diagonalized by inserting the Bloch wave ansatz for the NPs polarization vectors (Cartesian index $\mu$) $P_{a\mu}(\mathbf{r}_n, \mathbf{q}, \omega) = c_{a\mu}(\mathbf{q}, \omega)e^{i\mathbf{q}\cdot\mathbf{r}_n}$ into Eq. 1 yielding

$$c_{a\mu}(q, \omega) = \sum_b \alpha_b(\omega) \sum_{n'v} G_{a\mu}^{by}(n - n', \omega) e^{-i\mathbf{q}\cdot\mathbf{r}_{n'}} c_{b\nu}(q, \omega)$$

Noting that the sum on the right-hand side is independent of $n$ due to the translational invariance of the lattice we can finally write

$$c_{a\mu}(q, \omega) = \sum_{bv} \alpha_b(\omega) \sum_n G_{a\mu}^{by}(n, \omega) e^{i\mathbf{q}\cdot\mathbf{r}_n} c_{b\nu}(q, \omega).$$

Consequently, SPR in periodic lattices of NPs can be found by evaluating the minima of $\det(1 - D(q, \omega))$.

**Movie S1: Electric field propagation along a particle chain for excitation of 1.59 eV.** Movie captured from FDTD simulation, in which a dipole source is placed on the end of the plasmonic polymer and the energy transport along the chain can be tracked by the wave packages traveling according to the highest group velocity (4–6 particles).

**References**

1. Steiner, A.M.; Mayer, M.; Seuss, M.; Nikolov, S.; Harris, K.D.; Alexeev, A.; Kuttner, C.; König, T.A.F.; Fery, A. *ACS Nano* 2017, 11, 8871–8880.
2. Slaughter, L.S.; Willingham, B.A.; Chang, W.-S.; Chester, M.H.; Ogden, N.; Link, S. *Nano Letters* 2012, 12, 3967–3972.
3. Willingham, B.; Brandl, D. W.; Nordlander, P. *Applied Physics B* 2008, 93, 209–216.
4. Novotny, L.; Hecht, B., *Principles of Nano-Optics*. Cambridge University Press: 2006.