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Multimodal Plasmonics in Fused Colloidal Networks

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Abstract

Harnessing the optical properties of noble metals down to the nanometer-scale is a key step towards fast and low-dissipative information processing. At the 10-nm length scale, metal crystallinity and patterning as well as probing of surface plasmon (SP) properties must be controlled with a challenging high level of precision. Here, we demonstrate that ultimate lateral confinement and delocalization of SP modes are simultaneously achieved in extended self-assembled networks comprising linear chains of partially fused gold nanoparticles. The spectral and spatial distributions of the SP modes associated with the colloidal superstructures are evidenced by performing monochromated electron energy loss spectroscopy with a nanometer-sized electron probe. We prepare the metallic bead strings by electron beam-induced interparticle fusion of nanoparticle networks. The fused superstructures retain the native morphology and crystallinity but develop very low energy SP modes that are capable of supporting long range and spectrally tunable propagation in nanoscale waveguides.

Surface plasmons (SPs), which are collective oscillations of conduction electrons, are regarded as a promising gateway to on-chip sub-wavelength electro-optical devices.¹ Studies of SPs in noble metals have revealed that light energy can be confined in volumes of deep sub-wavelength dimensions² or propagated in metallic stripes¹ and grooves³ over tens of

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Author contributions

E.D., M.B., C. G. and S. M. conceived the experiments. G. K. L. and M.L. synthesized the nanoparticles and A.T. and M. L. prepared PNN suspension and TEM samples. M.B. performed and processed EELS experiments. C.G. and A.T. developed the model and implemented the simulation codes. A.T., M.B., C.G. and E.D performed data and simulation analysis and prepared the figures. All co-authors contributed to the writing of the article.

Additional information.

Supplementary information is available in the online version of the paper. (Materials and Methods. Figures S1-S9. Theoretical model and numerical simulation of EELS signal. Statistical correlation between SP modes and topological features. Principal Component Analysis. Movie of the EELS images as the probing energy scans from 3.0 to 0.3 eV).

Competing financial interests

The authors declare no competing financial interests.

micrometers. The appealing prospects of merging both properties into integrated structures and so of further pushing the limit of plasmonics towards atomic-scale devices face significant challenges in high fidelity fabrication and sub-nanometer-scale characterization of electromagnetic fields. In this regard, crystalline noble metal colloids act as a generic platform to tailor plasmonic properties in extremely small volumes near well-defined crystallographic surfaces, which has opened the way to efficient sub-wavelength propagation with significantly reduced dissipation, nanometer-scale confinement of the electromagnetic field and quantum plasmonics.⁴⁻⁶ SP modes in individual SP-bearing nanoparticles (NPs) can be designed by controlling their morphology, such as crystalline 1D nanowires,⁷ 2D ultrathin platelets^{8,9} or 3D dendritic NPs,¹⁰ which directly shapes spatially and spectrally the SP local density of states (SP-LDOS). Alternatively, new SP modes emerge by tuning the inter-particle dipolar SP coupling in dimers or linear arrays.¹¹ More complex assemblies are conveniently produced by self-assembling small nanoparticles¹² into superstructures such as chains¹³ and chain networks,^{14,15} 2D sheets¹⁶ or 3D assemblies.^{17,18} The small particle size and interparticle gap lead to large electromagnetic field enhancement yet long-range delocalization is intrinsically limited by the capacitive nature of the SP coupling.¹¹ The control of the conductive connectivity of possibly crystalline building blocks appears as a challenge of paramount importance for higher order plasmonic architectures.^{19,20}

In this Article, we show that ultimately narrow waveguiding structures are obtained by converting the capacitively coupled SPs in assemblies of strongly interacting NPs into conductively delocalized SP modes in continuous crystalline structures that retain the native morphology of the complex self-assembled blueprint. We prepare fused metallic bead strings by electron beam-induced interparticle melting of self-assembled 10-nm Au nanoparticle chain networks. In such networks of ultrathin chains, mapping the plasmon field and theoretically predicted SP-LDOS confinement²¹ is an experimental challenge. Here, we use monochromated electron energy loss spectroscopy (EELS) to reveal the spatial and spectral distribution of the SP-LDOS that fully characterize the modal behavior of our complex fused nanoparticle networks.^{8,22-26} We demonstrate that the fused superstructures tailor the SP-LDOS with an unprecedented spatial resolution and a convenient spectral addressability. The SP-LDOS is shown to be tightly confined within a few tens of nanometers around the NPs along highly contrasted and energy-dependent hot spot patterns that suggest a nanoscale spatial and spectral input/output addressability of light energy in these fused chain networks. Moreover, we observe the emergence of SP modes with energy as low as 0.38 eV (3200 nm equivalent photon wavelength) that are suitable for long range propagation in nanoscale-wide waveguides, near-IR sensing, light energy up-conversion or localized heat sources. These findings of SP-LDOS design for passive information transport echo new concepts that have been put forward for active optical information processing using colloids, such as logic gate devices based on interferential engineering in coupled colloids²⁷ or on the design of the SP local density of states (SP-LDOS) in large crystalline colloids.⁹ Our results suggest that the fused chains are ideal objects to explore crystalline plasmonic circuits at the limit between classical and quantum behavior.

Monodisperse gold nanoparticles, 12 nm in diameter, are prepared by the standard citrate reduction of gold tetrachloroaurate(III) and undergo a spontaneous self-assembly into

complex yet well-reproduced extended plasmonic nanoparticle networks (PNNs) upon addition of an adjusted amount of mercaptoethanol (MEA) following the protocol detailed in reference ¹⁴ and summarized in Methods.²⁸ PNNs are micrometer-sized reticulated networks of single-particle chains comprising typically 10-20 crystalline nanoparticles between nodes and thousands of particles overall and a 1-nm interparticle gap filled with MEA (Fig. S1). For EELS experiments, the PNNs are deposited on ultrathin amorphous SiN_x membranes, briefly exposed to an O₂ plasma in order to remove the MEA capping layer, and rapidly introduced into the transmission electron microscope (TEM). Significantly, in the absence of the O₂ plasma treatment, the PNNs are stable under an 80-100kV electron beam allowing detailed structural characterization (Figs. S1 and S2A). However, after the plasma cleaning, a near instantaneous fusion of the metal is selectively triggered in the narrow interparticle gap regions (Figs. 1A-B). The native self-assembled PNNs are thus converted *in-situ* into continuous and crystalline metallic bead strings that retain the network morphology (Fig. S2). We ascribe the localized melting of metallic nanoparticles to an enhanced local electric field in gap regions induced by the electron irradiation.^{29,30}

EELS maps of fused PNNs are recorded in scanning TEM mode at 80 kV by using a modified Spectrum Imaging technique ³¹ detailed in Methods.²⁸ After data processing, 0.1 eV energy windows around the plasmon peaks of interest are used to map the EELS intensity in each pixel. In Figure 1C, the local spectra of two specific locations, I and II, near the fused particle loop shown in Fig. 1B, are compared to the bulk extinction spectrum of the pristine, non-fused, PNNs in aqueous suspension (black dotted line). All three spectra share a low intensity peak located at 2.45 eV (i.e. 520 nm), characteristic of the transverse SP mode of single particle chains and originating in the SP mode of the isolated 12-nm Au nanoparticles.¹⁴ The uniaxial coupling of the localized SPs in the non-fused chains results in the emergence of lower energy modes that are inhomogeneously combined into the broad peak centered at 1.85 eV of the extinction spectrum. This longitudinal peak is accounted for by considering an average 1 nm interparticle gap filled with MEA and citrate molecules of average index 1.6.¹⁴ Interestingly, after fusion, the EELS spectra shown in Fig. 1C also present a second low energy peak, although its maximum is markedly red-shifted to 1.61 (position I) or 1.11 eV (position II). The corresponding EELS maps in Figs. 1D-F illustrate the spatial distribution of these three SP modes along the particle loop. The transverse mode (2.45 eV) appears to be strongly and uniformly confined along the entire contour (Fig. 1D). In contrast, the longitudinal modes exhibit a more pronounced modulation with the 1.61 eV resonance concentrated across the vertical diameter of the loop and the 1.11 eV mode predominantly distributed along the horizontal diameter with a maximum at the tip of the chain. These spatial modulations are reminiscent of other higher order longitudinal SP modes observed by near-field probe techniques in nanowires.^{4,7,32}

In order to get a better insight into the spectral and spatial evolution of the SP modes in the fused PNN, we have developed a model and a numerical tool dedicated to the simulation of EELS experiments and based on the Green Dyadic Method (GDM). We consider a swift electron beam probing the near-field of a linear nanoparticle chain in normal incidence at location R₀ (Fig. 2A). In such a configuration, EELS maps and spectra can be computed from the LDOS projected onto the electron trajectory (Z axis) by calculating the total

Coulomb force work accumulated by the electron.³³ We formulate an equivalent quantum approach in which the impinging electrons that interact with the plasmonic structure undergo a state change and yield a $\hbar\omega_0$ quantum of energy. This transition generates an effective dipole oscillation at the loss frequency ω_0 . Since its field linearly derives from the Green dyadic response of the nanoparticle, a formal relation between the average energy lost per electron and per unit time, ΔE_{EELS}^z , and the imaginary part of the (zz) component of the Green dyadic tensor, $S_{zz}(\mathbf{R}_0, \mathbf{R}_0, \omega_0)$, can be easily established:²⁸

$$\Delta E_{EELS}^z(\omega_0) = \frac{e^2 \hbar^2 A^2}{8m^2 \omega_0} \left| \mathbf{m} \{ S_{zz}(\mathbf{R}_0, \mathbf{R}_0, \omega_0) \} \right| \quad (1)$$

where m and e are the electronic mass and charge, A accounts for the electron probe resolution and has the dimension of an inverse length and ω_0 is the angular frequency of the energy loss.

Therefore, the knowledge of the field propagator $S_{zz}(\mathbf{R}_0, \mathbf{R}_0, \omega_0)$ associated with any nanoparticle superstructure suffices to compute the EELS maps and spectra. In general, numerical simulations are performed on finely discretized structures as shown in Figure 2. We first examine the spectral evolution of the EELS signal of a linear chain comprising an increasing number of fused nanoparticles (Fig. 2C). For a dimer of fused particles, two peaks are visible. The high energy transverse mode (2.40 eV) corresponds to the SP mode of the isolated particle (2.42 eV) that has undergone a marked attenuation and a small red-shift. The energy position of this transverse mode remains essentially unchanged as the number of fused particles increases, whereas the attenuation proceeds monotonously. Noticeably, the low energy peak rapidly shifts from 2.10 eV, for the dimer, towards lower energy, without significant broadening. This is very different from the case of self-assembled, non-fused particle chains for which the low energy resonance rapidly saturates at a value that depends on the gap size and nature of the capping layer.¹⁵ For MEA-capped PNNs, the limit is ca. 700 nm for an average gap size of 1 nm (Fig. 1C).¹⁴ The observed linear increase of the wavelength of the peak maximum with the aspect ratio of the fused chain (Fig. 2C, inset) is similar to the classic behavior of Au nanorods (Fig. S5).³⁴ This result strongly suggests that the large red-shift observed in the EELS spectra of Fig. 1C, but not in the absorption spectrum of native PNNs, can be ascribed to the local fusion of neighboring particles. Moderate fusion between nanoparticles produces enough metallic contact to restore topological order and to open new conductive SP channels. The resulting marked low-energy shift of the modes indicates an increased physical size of the supported coherent excitations. A similar influence of conductive coupling was observed in nanorods or tip-to-tip triangular prism dimers upon breaking the metallic bridge.^{19,20} The calculation of the plasmonic transmittance through fused nanoparticle chains (Fig. S3) further underpins the efficient guiding of optical information in fused PNNs. It is noteworthy that the fused bead strings sustain fewer and broader SP modes than the sharp resonator behavior of perfectly straight and smooth nanorods because of the residual surface corrugation and general morphological complexity.

Applying our simulation tool to more realistic structures, we constructed a model of the sample in Fig. 1B, where each particle is assimilated to a sphere fused with its nearest

neighbors according to the projection given by the TEM image. The entire structure volume is discretized on a face centered cubic mesh in order to better account for the bead string morphology (Fig 2B). The agreement between the experimental EELS (Figs. 1D-F) and simulations maps (Figs. 1G-I) is remarkable. In particular, the homogeneous contour of the 2.45 eV map and the strong confinement of the EELS signal within 15 nm from the loop contour can be observed in both experimental (Fig. 1D) and simulated (Fig. 1G) maps. Equivalently, the overall EELS signal distribution as well as the specific localized intensity maxima of the 1.61 eV (Figs. 1E and 1H) and 1.11 eV (Figs. 1F and 1I) maps coincide. The simulated EELS spectra present three characteristic peaks at 2.37 eV (Fig. 1J), 1.67 eV (Fig. 1K) and 1.04 eV (Fig. 1L) in close match with the recorded data.

Figure 3A features a larger PNN fragment comprising several loops and chains of fused nanoparticles. The EELS map of the transverse SP mode recorded at 2.40 eV (Fig. 3B) confirms its extreme and homogeneous confinement along the edge of the entire structure, in agreement with earlier calculations.²¹ Since this high energy mode is impervious to the effect of the limited fusion of the particle chains, we computed the EELS map shown in Fig. 3C by describing each sphere with a dipolar polarizability.²¹ Despite this approximation, the simulated map reproduces the experimental data with fine details, including the areas of higher EELS intensity. These maps can be more quantitatively analyzed by comparing two intensity profiles extracted along the same line (Fig. 3D). The experimental EELS intensity (blue histogram) and the simulated signal (continuous orange line) overlap exactly. In particular the decay of the EELS signal away from the particle edges is accurately described. Figures 3E and 3F accumulate cross-sections of the near-field decay range taken horizontally inside the black box of Fig. 3A and with the distance origin chosen at the particle edge. Both experimental and simulated decay curves confirm that the confinement of the LDOS at this energy is on the order of 15 nm. Our results suggest that the decay rate follows a slower trend than a r^{-3} dipolar power law profile that could be expected from the classical description of the near-field near the surface of a single nanoparticle,³⁵ for example in fluorescence experiments.³⁶ Among possible causes of this variation, the complex morphology of the fused PNN places any point in the near-field under the influence of a large number of particles and the EELS signal in a given position accumulates the energy loss along the entire electron trajectory rather than in a single point-like location.

With small bead strings sustaining modes with energy as low as 1 eV (1240 nm), we anticipate that larger fused PNNs hold a strong potential for long-range propagation of ultimately confined, low energy SP modes. Fig. 4A shows EELS spectra recorded down to 0.2 eV in locations I to IV near the fused PNN of Fig. 3A. The ubiquitous 2.45 eV transverse resonance is weak in comparison to the multimodal features observed between 1.5 and 0.2 eV, the spectral details of which vary from one location to another. Linear or kinked chains in locations II and III yield essentially a single peak around 0.7-0.9 eV, while branched and looped topologies in locations I and IV sustain a multiple peak pattern with dominant features at 0.4 and 1.2 eV. A systematic analysis of EELS spectra associated with basic topological patterns confirms that Y-shaped junctions, free-end chains and linear fragments produce specific SP-LDOS resonances around 0.4, 0.9 and 1.5 eV (Figs. S6-S8).²⁸ Remarkably, similar findings were reported for calculated far-field extinction spectra of linear, kinked, branched and looped fragments of aqueous PNN suspensions.¹⁴ The

multiple resonances of the longitudinally coupled SP mode occurred at higher energies (1.55-1.8 eV) since the chains were not fused but could nevertheless be observed due to the large local refractive index created by the organic capping layer.²⁸ The spectral features in the longitudinal SP modes are therefore, in part, determined by the topology that pre-exists in the native PNN and are preserved in the fused bead strings.

Interfacial fusion further enhances the coupling between particles by creating continuous, conductive structures that lead to the long range delocalization indicated by the extremely low energy modes probed in EELS. The spatial extension of each of these modes was characterized by mapping the EELS intensity as presented in Figs. 4B-F (see also Fig. S7). The well-resolved maps reveal that the EELS intensity or, equivalently, the SP-LDOS at the chosen energy is tightly confined near the narrow particle chains. Moreover, the intensity extrema present marked spatial variations when the 0.1 eV-wide energy window is tuned between 1.2 and 0.4 eV. The transverse confinement naturally loosens as lower energies are probed. The apparent transverse decay length of the EELS signal is *ca.* 20 nm at 1.21 and 1.00 eV (Fig. 4B and 4C) but reaches *ca.* 50 nm at 0.60 and 0.38 eV (Fig. 4E and 4F). The multimodal behavior of the fused PNN creates a collection of high intensity spots, 30 to 50 nm in diameter, that are located at small loops (Figs. 4B, right side or 4E top left), at successive spots along the central chain (Figs. 4F, 4C, 4D, 4E), inside the large loop (Figs. 4B, 4D, 4F) or at the very end of lateral chains (Fig. 4E). The selective spectral tuning of the spatial distribution of SP-LDOS in PNN, which was predicted for visible wavelengths in pristine networks,²¹ can be extended, after fusion, to the mid-IR range.

Interestingly, in some cases, an EELS signal that continuously follows the colloidal superstructure is measured for some energies (for example 1.21, 1.00 and, to a lesser extent, 0.38 eV) while other energy windows clearly segregate the network into resonant and non-resonant areas (for example 0.60 and 0.79 eV). Optically, the fused structures can be considered as 12-nm wide SP waveguides with complex topology in which some SP modes promote energy propagation along metallic bead strings, when other ones confine it in specific sub-20 nm fragments. Indeed, GDM near-field calculations presented in Fig. S3 confirm the significant transmittance of fused NP chains upon excitation by a dipole source placed near the proximal end of the chain. The transmittance spectrum exhibits clear modal features that reflect the SP-LDOS spectrum. When excited at the wavelength of a low-energy resonance maximum, the transmitted near-field intensity at 10 nm above and away from the distal end can exceed 70% of the intensity at the input. Although the PNN fragments displayed are small, micrometer-long examples show similar properties (See Fig. S9) and the extent of fully formed PNN can reach a globular size of several micrometers in diameter opening the way to meso- to nanoscale interfacing. In this context, regions where the EELS signal shows a maximum (*i.e.* large SP-LDOS) can be conceived as entry points to address the waveguiding networks optically³⁷ or inelastically using a low bias tunneling current.^{38,39}

In conclusion, this work demonstrates sculpting SP-LDOS with unprecedented spatial resolution and a convenient spectral addressability. In particular, fused PNNs gather several desirable attributes for ultimate scale optical applications. The self-assembled PNNs are topological blueprints that can be subsequently fused into multimodal plasmonic

waveguides offering nanoscale lateral confinement and micrometer scale transport tracks. The initial self-assembly step sets the spatial SP-LDOS landscape by defining the topology of the nanoparticle ensemble. Next, the local fusion spectrally converts the coupled local SP modes into extended SP channels and reduces the overall disorder. Our approach is general and can be applied to the fusion of better ordered superstructures. Indeed, the complexity of self-assembled PNN could be harnessed into more regular constructs by precisely directing the self-organization of crystalline metal building blocks in lithographically designed templates.^{18,40}

The wealth of high and low energy SP modes bound in the fused chain networks opens the possibility of spectral addressing and spatial control of light energy at the nanometer length scale that can be exploited in a number of areas. The strong and addressable confinement of the near-IR resonances could trigger highly localized surface-enhanced IR absorbance (SEIRA) and emission of single near-IR fluorophores such as lanthanide-containing molecules⁴¹ or polyaromatic hydrocarbons⁴² and thus contribute to a more efficient up-conversion of light energy in photovoltaic devices. They could equally improve the interfacing of other near-IR active two-dimensional materials such as graphene nanoribbons.^{43,44} Complex colloidal architectures such as PNNs or their future templated derivatives could also be engineered as localized heat sources⁴⁵ or metamaterials¹⁷ for which the fusion post-treatment could advantageously tune the SP modes to reinforce the field enhancement or modulate the refractive index at chosen wavelengths.

Finally, PNNs are ideal systems to explore the limit between classical and quantum plasmonics in an extended ensemble of 10-nm nanoparticles spaced by sub-1 nm gaps that can be further decreased upon controlled fusion.^{46,47} We show that colloidal self-assembly fosters a promising route to demonstrate concepts of quantum plasmonic circuitry that might even be driven down to atomic scale electro-optical addressing in atomic metal chains.⁴⁸

Methods

Nanoparticle chain self-assembly

Plasmonic Nanoparticle Networks (PNN) were synthesized by the method reported in references^{14,49}. Briefly, Au nanoparticles were freshly prepared by the citrate reduction method at a citrate: $[\text{AuCl}_4]^-$ molar ratio of 5.2: 1 and diluted to the required concentration with 18 M Ω .cm deionized water. The average diameter of the Au nanoparticles was 12.0 ± 1.1 nm. The assembly of the PNN was performed at room temperature by adding 2-mercaptoethanol ($\text{HS}(\text{CH}_2)_2\text{OH}$) to the diluted Au nanoparticle solution at a Au nanoparticles: MEA molar ratio of 1: 5000. The nanoparticle chain assembly is characterized by a color change from pink to purple as the coupled modes emerge. It was monitored by UV-Visible spectrophotometry until completion within 24 to 48 h after mixing.

TEM sample preparation

A 10 μL droplet of fully formed PNN suspension was drop-casted onto 10-nm thick silicon nitride membranes and left to dry in clean environment. A series of 1-minute O_2 plasma

cleaning steps were performed to eliminate the mercaptoethanol and citrate capping moieties. Structural TEM analysis was performed using a Philips CM20FEG microscope operated at 100 kV. Particular care was taken to adjust the plasma cleaning step to avoid any damage or modification of the chain morphology compared to unprocessed PNN. Complementary SEM observations were performed on a Zeiss 1540XB Gemini microscope.

Electron energy-loss spectroscopy (EELS)

EELS was performed in scanning TEM (STEM) mode using an FEI Titan TEM with Schottky electron source. The microscope was operated at 80 kV, and a STEM convergence semi-angle of 13 mrad was used to form a probe with a diameter of approximately 1 nm. A Wien-type monochromator dispersed the electron beam in energy, and an energy-selecting slit formed a monochrome electron beam with typical full-width at half-maximum values of 70 meV. A Gatan Tridiem ER EELS detector was used for EELS mapping and spectroscopy, applying a 12 mrad collection semi-angle. EELS data was acquired with a modified binned gain averaging routine:³¹ individual spectra were acquired in 40 ms, using 8 or 16 times on-chip binning. The detector channel-to-channel gain variation was averaged out by constantly changing the readout location and correcting for these shifts after the EELS acquisition was finished. A high-quality dark reference was acquired separately, and used for post-acquisition dark signal correction. Spectra were normalized by giving the maximum of the zero-loss peak (ZLP) unit value, and the ZLP background signal was removed by fitting and subtracting a high-quality background spectrum.

EELS mapping

EELS maps were obtained with the Spectrum Imaging technique: scanning a small electron probe with an approximate diameter of 1 nm in a rectangular raster of pixels, while at each pixel an EELS spectrum is collected and stored. After data processing as described above, 0.1 eV energy windows around the plasmon peaks of interest were used to image the EELS intensity in each pixel in linear scale. The EELS intensity maps were colour-coded to a temperature scale.

Simulations

Our model formulates the energy yielded by a swift electron passing in the vicinity of a metallic object in terms of an effective dipole oscillating at the loss frequency. The average power transferred to the plasmonic system is computed by the Green Dyadic Method in which the whole dyad $S(\mathbf{r}, \mathbf{r}', \omega_0)$ of the considered system is computed by solving a Dyson's equation sequence.⁵⁰ In order to optimize the representation of the complex curved surfaces of the fused bead chains, the volume of the system is discretized in a face centered cubic lattice. This method allows the numerical computation of EELS maps for a given energy, $\hbar\omega_0$, and spectra for a fixed position, $\mathbf{R}_0$.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1. Spatial and spectral characterization of plasmon-mediated electron energy-loss in the vicinity of a fused Au nanoparticle chain

(A) Scheme of mercaptoethanol-driven PNNs self-assembly and their conversion into continuous bead strings by electron-beam induced welding. (B) TEM image of a short looped Au particle chain after local fusion. The individual particles still display their pentatwinned structure. Markers (I) and (II) indicate the position where loss spectra displayed in (C) are recorded. (C) EELS spectra recorded in position (I), blue, and (II), red. The absorption spectrum of the starting particle networks suspended in water is displayed by the black dotted line. The equivalent photon wavelength axis is computed as $\lambda(\text{nm}) = 1240/\text{Energy}(\text{eV})$. (D-F) Experimental and (G-I) simulated EELS maps recorded at (D, G) 2.45 eV, (E, H) 1.61 eV and (F, I) 1.11 eV. In (G-I), the maps are calculated in a plane 10 nm above the nanoparticles and the TEM outline of the fused particle chain is overlaid. (J-L) Calculated EELS spectra obtained from equation (1) at locations close to (I) and (II) and cross-marked in (G-I) respectively. All scale bars are 20 nm.

Fig. 2. Numerical simulation of EELS spectra of plasmonic nanoparticle chains

(A) Schematic of a swift electron beam impinging at $R_0 = (X_0, Y_0, Z_0)$ to probe the near-field of a linear nanoparticle chain deposited on a thin membrane. The inelastic energy loss process is computed in a point located along the chain axis at a distance $2a$ from the terminal particle center in the plane $Z_0 = 2a + 10\text{nm}$ with “ a ” the nanoparticle radius (see star marker). (B) Schematic of the discretized face centered cubic 3D model of the fused particle chain shown in Fig. 1B. (C) Simulated EELS spectra of an isolated 12-nm Au nanoparticle (black) and a series of fused linear chains composed of two (red), three (blue) and four (purple) Au nanoparticles. The fused overlap corresponds to 17% of the diameter. Inset: Linear evolution of the low energy peak position as a function of the fused chain aspect ratio, $L_{\text{chain}} / 2a$, with L_{chain} the total chain length. The continuous line is a linear fit to the data.

Fig. 3. Extreme confinement of the 2.4 eV plasmon mode in complex PNN

(A) TEM image of a branched and looped Au nanoparticle chain after undergoing in-situ electron beam induced fusion. (B) EELS intensity map recorded at 2.4 eV corresponding to the maximum of the transverse plasmon mode. (C) Simulated EELS map at 2.4 eV computed in the discrete dipole approximation. The elastic electron scattering is taken into account by nulling the EELS signal in the position of the nanoparticles. Scale bars are 50 nm. (D) Experimental (blue histogram) and simulated (orange line) single line cross-sections extracted from (B) and (C), respectively, along the dotted line shown in (C). (E) Experimental and (F) simulated spatial decay of the EELS intensity extracted from horizontal cross sections in maps (B) and (C) respectively in the region marked by the thin black box in (A). X error bars in (E) represent the pixel size.

Fig. 4. Mapping of low energy plasmon modes in complex PNN

(A) EELS spectra recorded in positions (I) to (IV) near the PNN structure shown in Fig. 3(A). The equivalent photon wavelength axis is computed as $\lambda(\text{nm}) = 1240/\text{Energy}(\text{eV})$. (B-F) EELS maps recorded from the well-separated resonance features at 1.21, 1.00, 0.79, 0.6 and 0.38 eV with a 0.1 eV pass band width. Scale bars are 50 nm. Color scale is similar to Fig. 3B.