Inhibition of multipolar plasmon excitation in periodic chains of gold nanoblocks

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Abstract: Periodically corrugated chains of gold nanoblocks, fabricated with high precision by electron-beam lithography and lift-off techniques, were found to exhibit optical signatures of particle plasmon states in which relative contribution of longitudinal multipolar plasmons is significantly lower than that in equivalent rectangular gold nanorods. Plasmonic response of periodic chains is dominated by dipolar plasmon modes, which in the absence of multipolar excitations are seen as background-free and spectrally well-resolved extinction peaks at infrared (IR) wavelengths. This observation may help improve spectral parameters of IR plasmonic sub-wavelength antennae. Comparative studies of plasmon damping and dephasing in corrugated chains of nanoblocks and smooth rectangular nanorods are also presented.

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OCIS codes: (240.6680) Surface plasmons; (260.3910) Metals, optics of; (160.4760) Optical properties

References and links

1. Introduction

Optical properties of noble metal nanoparticles are dominated by localized surface plasmons (LSP) [1], recognizable from resonant extinction peaks in the elastic light scattering spectra, and having spatial field modes strongly localized at the metal’s surface. The resonant scattering and field enhancement are attractive features for nanophotonics [2, 3, 4], single molecule detection [5, 6], high-resolution microscopy [7, 8], development of metallic emitters of visible radiation [9], bio-sensing [10, 11, 12], and terahertz (THz) imaging [13, 14]. Smallest nanoparticles whose dimensions do not exceed few tens of nanometers, typically exhibit LSP resonances at visible wavelengths and have predominantly dipolar spatial modes. In larger nanoparticles the fundamental (lowest frequency) LSP resonance also has a dipolar spatial mode whose central wavelength roughly scales with the nanoparticle size, and in addition, LSP resonances with multipolar spatial modes may evolve in a broad spectral range, resulting in new resonant scattering peaks riding on a spectrally broad background [15]. Practical spectral tuning of LSP resonances is achieved by tailoring the size and shape of nanoparticles, and is especially versatile with nanorods having rectangular or circular cross-sectional shape. Elongation of nanorods leads to so-called LSP shape resonances, and allows selective excitation of longitudinal plasmon (LP) modes by optical field polarized along the axis of elongation. Plasmonic applications aimed at infrared (IR) wavelengths would generally require an increase in the nanorod length. However, this leads to an increased contribution of multipolar LP modes [15, 16], which may be not desired in plasmonic applications that require spectral selectivity. In this work we propose and implement a simple design for elongated nanoparticles that allows a substantial inhibition of multipolar plasmonic modes, while retaining dipolar modes essentially unaffected. The basic idea of this proposal can be understood by recalling that multipolar LP modes of smooth nanorods have field patterns reminiscent of a standing wave oriented in the direction of nanorod elongation. In smooth nanorods the standing-wave modal patterns (each mode contributing to extinction at a certain spectral position) must be commensurate with the nanorod length. Among the allowed LP modes, the lowest-order and lowest-energy longitudinal mode will be predic-
Fig. 1. (a) Geometric parameters of gold nanoparticles on a dielectric substrate: (1) a chain of connected nanoblocks, (2) a straight nanorod. The side and diagonal lengths are given in nanometers, \( N \) is the number of chain/rod segments along the \( y \)-axis direction. All dimensions are given in nanometers, the decrease in the total length of the nanoblock chain due to a slight overlap, \( w \), between the nanoblocks is ignored. Nanoparticles are attached to a thick dielectric substrate whose thickness is drawn out of scale in the Figure. (b) Top-view SEM image of chain of nanoblocks with \( N = 3 \). The yellow dashed line shows the outline of designed nanoblocks, the scale bar corresponds to 100 nm. In optical studies incident radiation was polarized linearly along the \( y \)-axis for predominant excitation of LP modes.

Inantly dipolar, while higher-order modes will be multipolar. On the other hand, if a periodic corrugation (such as variation of transverse size) is intentionally imposed on the nanorod, excitation of longitudinal modes that are incommensurate with both the nanoparticle length and the period of corrugation will be inhibited. This prediction was verified in the present work by fabricating chains of diagonally-oriented, overlapping gold nanoblocks, and comparing their plasmonic scattering spectra with those of smooth rectangular nanorods. As expected, chains of nanorods exhibit much weaker spectral signatures of multipolar LP modes due to their periodically corrugated shape. In addition, comparison between the parameters of fundamental dipolar LP modes in both kinds of nanoparticles is reported. We demonstrate that chains of nanoblocks, despite their somewhat larger volume, exhibit similar radiative plasmon damping as smooth nanorods. At the same time, periodic nanoparticle chains, same as nanorods, allow tuning of the plasmonic response by scaling the chain length, and in practice allows one access the IR spectral regions.

2. Samples and their fabrication

Layout of the investigated gold nanoparticles is illustrated schematically in Fig. 1(a). The structure labeled \( l \) is composed of rectangular gold nanoblocks with side length of \((100 \times 100 \times 40)\,\text{nm}^3\), aligned diagonally into chains of \( N \) nanoblocks, with a small overlap \( w \) between their nearest corners. The chain has an elongated form-factor and is periodic along the \( y \)-axis with period \( l = (141 - w/2) \,\text{nm} \). Fig. 1(b) shows Scanning Electron Microscopy (SEM) image of the fabricated nanoparticle comprising three nanoblocks. The fabrication process and structural characteristics of nanoparticles will be discussed later. For comparison with rectangular nanorods whose optical properties are relatively well-studied, nanorods labeled 2 in Fig. 1(a) were also fabricated. The nanorods have square cross-section with side length in the \( x - z \) plane.

#88640 - $15.00 USD  Received 16 Oct 2007; revised 21 Nov 2007; accepted 25 Nov 2007; published 29 Nov 2007  (C) 2007 OSA 10 December 2007 / Vol. 15, No. 25 / OPTICS EXPRESS  16529
of 40 nm, and a total length in the $y$−axis direction of $l = 141N$. Hence, nanoblock chains and nanorods with the same $N$ have nearly identical lengths. In the following we will refer to the two categories of nanoparticles simply as “nanoblocks” (or “chains of nanoblocks”) and “nanorods”, respectively.

The fabrication was aimed at obtaining large ensembles of periodically arranged nanoparticles with identical design parameters. A similar fabrication procedure was used in our earlier works [9, 12, 17, 18]. First, planar patterns of nanoparticle arrays were defined using an EBL system (ELS-7700H, Elionix Co., Ltd., Japan) on a thin film of co-polymer resist (ZEP-520a, Zeon Co., Ltd., Tokyo, Japan), spin-coated on $(10 \times 10)$ mm$^2$ sapphire substrates (Shinkoshya Co., Japan). After the exposure the substrates were developed in a standard developer (Zeon Co., Ltd., Japan). Subsequently, 2 nm thick Cr and 40 nm thick Au films were sputtered on the substrates and lift-off was performed by immersion in sonicated acetone and resist remover (Zeon Co., Ltd.) solutions for 5 min. As a result, substrates with identically oriented, nanoparticles having the same length $N = 1, 2, \ldots, 25$ were prepared. In order to reveal possible influence of narrow necks on the LSP properties of nanoblock structures, three series of nanoblock samples with different neck widths of $w = 4.4$, 8.8, and 13.2 nm were fabricated.

3. Results and discussion

3.1. Structural quality of the samples

Prior to discussing optical properties of the fabricated nanoparticles, it is relevant to briefly examine their structural parameters and correspondence with the idealized models shown in Fig. 1.

Structural inspection of the samples was performed by SEM using JSM-6700FT (JEOL). As emphasized in Fig. 1(b), shapes of the actual nanoparticles deviate from the initial design. The deviations seen in the SEM images involve rough sides and rounded corners of the nanoblocks. Previously we have conducted careful analysis of plasmonic extinction spectra in gold nanorods, fabricated using the same method as in the present study. It was determined, that despite some irregularities seen in SEM images, difference between the design and actual lengths of nanorods was in the range from 0.625 to 1.93 nm, which corresponds to the thickness of about 4 to 12 atomic layers of gold [18]. This result allows to expect fabrication with similar accuracy in the present study as well. Height of the nanoparticles and quality of their top surface were inspected using Atomic Force Microscopy (AFM), and the average height of 40 nm, and a roughness of about 2 nm were found. Thus, despite some imperfections seen in SEM images, overall quality and uniformity the samples can be regarded as comparable to or higher than those reported before.

3.2. Optical properties

Optical extinction spectra of the samples were measured in transmission geometry using a Fourier-transform infrared (FTIR) spectrometer equipped with a microscope attachment (FT-IR, IRT-3000, Jasco) in the wavelength range of 660-4000 nm. In the measurements, areas with typical size of $(20 \times 20)$ $\mu$m$^2$ comprising about 1000 nanoparticles, depending on their size, were probed with the help of infrared microscope. The microscope uses a pair of confocal Cassegrainian reflection objectives with angular acceptance range of $16 - 32^\circ$ with respect to the optical axis. During the measurements the substrates were oriented perpendicular to the optical axis of the objectives.

Elongated nanoparticles exhibit so-called shape resonances in the LSP scattering spectra. These resonances can be recognized from distinct extinction peaks for different orientations of linearly-polarized incident radiation. For polarization parallel and perpendicular to the axis of elongation (coincident with $y$−axis in Fig. 1(a)), longitudinal plasmon (LP) and transverse...
plasmon (TP) modes are excited. Spectral position of TP and LP resonant modes generally depends on the size and shape of nanoparticles. In this study we will mainly focus on the LP modes and their transformation with nanoparticle length.

The FTIR spectrometer and microscope setup used for the measurements is equipped with unpolarized light source, which prevents selective excitation of purely LP and TP modes, except at visible and NIR wavelengths where it was possible to directly verify longitudinal or transverse origin of the spectral features by inserting a polarizer into the probing beam of the microscope during the measurements. Nevertheless, in our strongly elongated nanoparticles it was possible to identify the LP modes from their spectral position (at long wavelengths) even using unpolarized excitation. A further indirect proof of longitudinal nature of the modes was obtained from theoretical calculations.

Fig. 2. Extinction spectra of (a) nanoblocks, (b) nanorods.
3.2.1. Chains of nanoblocks

Figure 2(a) shows the measured LP extinction spectra of nanoblock structures comprised of different number of segments, \( N \). Each spectrum is dominated by two major extinction resonances. One of them occurs at a constant photon energy \( E = 1.75\text{eV} \) (wavelength of 0.71 \( \mu \text{m} \)) in all samples regardless of their length. We have verified polarization invariance of this peak’s position (i.e., nearly identical spectra were obtained for linear polarization corresponding to LP and TP modes). These findings indicate the fundamental (lowest frequency) mode of a single nanoblock as the origin of the LP peak.

Another major resonant extinction peak occurs at a lower photon energy (for example, \( E = 0.76\text{eV} \) (wavelength of 1.6 \( \mu \text{m} \)) for nanoparticles with \( N = 2 \)), and exhibits a red-shift with \( N \), completely tuning out of the observation range for \( N > 6 \). The approximate spectral position and the red-shift of this peak indicates fundamental LP mode of the entire multi-block nanoparticle as its origin. The two dominant peaks seen in LP extinction spectra can be thus tentatively ascribed to the two characteristic shape components – that of a single nanoblock, and of an elongated composite nanoparticle – in chains of nanoblocks.

We emphasize that spectral interval between the two of the above mentioned peaks has no other distinct features, such as minor resonances and broadband background, that might signify excitation of multipolar LSP resonances.

3.2.2. Smooth rectangular nanorods

Figure 2(b) shows the measured LP extinction spectra of rectangular nanorods. Resonant extinction peaks centered at a constant photon energy of \( E = 2.0\text{eV} \) (wavelength of 0.62 \( \mu \text{m} \)) can be seen for all nanorods regardless of their length. At lower photon energies, extinction peaks whose spectral positions are red-shifted with \( N \) are clearly visible. Although the presence of two major extinction peaks and their spectral behavior may look similar to those seen in the nanoblock structures, there are some important differences. Two dominant peaks are seen even for the shortest nanorods (\( N = 1 \)), with the low-energy peak centered at \( E = 1.3\text{eV} \) (wavelength of 0.95 \( \mu \text{m} \)). This occurs because nanorods with \( N = 1 \) are elongated nanoparticles with aspect ratio of 3.5, whereas equivalent nanoblocks are symmetrical with aspect ratio of 1. One can also notice that low-energy extinction peaks of nanorods in Fig. 2(b) appear to be asymmetrically broadened and ride on a wide background. One more difference from the spectra of chains of nanoblocks is the presence of weaker minor extinction peaks in the spectral interval between the two major peaks for longer nanorods (\( N \geq 4 \)). Similar peaks were observed previously in lithographically designed silver nanorods, and assigned to multipolar LSPs [15, 16]. The latter assignment is most likely valid in our case as well. In comparison to the nanoblock chains (Fig. 2(a)), smooth nanorods seem to exhibit a significant broadband background scattering, that is likely a consequence of a wide distribution and merging of multipolar LSP resonances. According to the earlier report [15], silver nanorods also exhibit a significant broadband background at equivalent spectral positions.

The above data make it obvious that chains of nanoblocks have better-resolved and background-free resonant LSP extinction peaks than smooth nanorods.

3.3. Spectral characteristics of LSP resonances

The observations described in Sect. 3.2 illustrate that both kinds of the investigated nanoparticles have spectrally constant, and length-tunable LP modes. Properties of the tunable LP modes, which are seen as major resonant peaks in the extinction spectra, are summarized in Fig. 3. In estimating parameters of the LP peaks in Fig. 2, they were fitted by a Lorentz function, which is commonly used in spectroscopy for representing homogeneously broadened resonances. Fig. 3(a) shows the central energy, \( E_c \), of the extinction peaks versus the number of
Fig. 3. Parameters of LP peaks versus the nanoparticle length deduced from spectra in the previous Figure: (a) central wavelength, (b) spectral width, (c) LP quality factor, and (d) dephasing time.

As can be seen, the lowest-energy LSP modes behave almost identically in chains of nanoblocks and smooth nanorods by decreasing monotonously with the total length. Chains of nanoblocks have only one length-tunable LSP mode, whereas smooth nanorods exhibit two such modes, denoted by the index $j = 1, 2$ in Fig. 3(a). In analogy with the existing interpretation [15, 16], in our case $j = 1$ represents the dipolar mode, whereas $j = 2$ represents the dipole-allowed multipolar LSP mode of the lowest order (most likely, the second multipolar mode to the lowest). This assignment is also supported by the results of theoretical modeling in Sect. 3.4. It is relevant to point out that $j = 2$ mode might not be the lowest-energy multipolar mode. Reexamining the extinction spectra shown in Fig. 4(b), one may conclude that noticeable asymmetry of the fundamental extinction peaks of nanorods may be due to the presence of weak high-energy spectral shoulders, possibly arising due to multipolar LSP modes. However, weakness of these features makes their quantitative identification difficult (likewise, even for modal peaks labeled $j = 2$, only their spectral position (but not width or resonance quality) could be determined reliably).

Below we will examine the tunability range and damping mechanisms of dipolar LSP modes. Full tunability range achieved with the fabricated gold nanoparticles extends beyond our experimentally available observation range in longer structures ($N > 7$). Nevertheless, it can be extrapolated that $E_c$ will reach the short-wavelength edge of the THz range ($\approx 0.012 \text{eV}$) in the
longest of the fabricated nanoparticles. This parameter may be important for applications like THz imaging.

Fig. 3(b) shows the spectral width, $\Delta E$ (FWHM), of the peaks extracted from their Lorentzian best fits, versus the number of nanoparticle segments. As can be seen, equivalent nanoblock and nanorod structures exhibit lowest-energy LSP modes with nearly identical spectral widths. Spectral width characterizes damping of the resonance and its quality factor, $Q = E_c / \Delta E$. These parameters are important in applications relying on coherent and incoherent interactions occurring in the regions occupied by the LSP near-field. Quality factors for the investigated samples are plotted in Fig. 3(c), and are very similar for nanoblock chains and nanorods with $Q \approx 4.5$, except for $N = 1$, when nanoblocks have somewhat higher quality factor than nanorods. The energy loss reflected by the quality factor occurs mostly due to the finite plasmon lifetime $T_1$, limited by radiative and non-radiative decay of plasmon population. For homogeneously broadened resonances, plasmon dephasing time can be determined as $T_2 = 2/\langle h\Delta E \rangle$. This expression includes the (radiative and non-radiative) plasmon lifetime $T_1$ and their “pure” elastic scattering described by a time constant $T_2^*$, such that $1/T_2 = 2/T_1 + 1/T_2^*$. Slower dephasing provides better spectral selectivity and promotes coherent interactions between the plasmonic near-field and surrounding species (e.g., molecules). Figure 3(d) shows dephasing time deduced by assuming predominantly homogeneous ensemble broadening. This assumption is validated by the high accuracy of fabrication process and a high homogeneous linewidth of the resonances concerned. As can be seen, dephasing is fastest in shorter nanoparticles, where the value of $T_2 \approx 5 - 6$ fs is close to that in bulk gold [19]. $T_2$ increases with the length, reaching about 20 fs for the longest nanoparticles studied. This value is close to the record-long dephasing times found earlier for LP modes at visible frequencies in small gold nanorods [19]. However, our findings must be treated with caution, since in longer nanoparticles length of the optical cycle corresponding to the LP resonance is also longer. Taking this fact into account, LP coherence is relatively short-lived in our samples, compared to that in [19]. This is also indicated the quality factors $Q \approx 4 - 8$, whereas the above study has reported $Q \approx 20$. From the dependence of $T_2$ on the length of nanoparticles in Fig. 3(d), one can infer that dephasing time comprises approximately constant number optical cycles, thus suggesting radiative plasmon damping as the dominant dephasing mechanism. Radiative losses are known to increase with volume of nanoparticle [20], which in our studies is relatively large, even for nanoparticles with $N = 1$. It is interesting to note, however, that although nanoblocks have 3.5 times the volume of nanorods, they exhibit similar dephasing times as nanorods. The most likely reason for this result is that despite the larger geometric volume, LSP modes of chains of nanoblocks are well-localized, and their modal volume is comparable to that of equivalent modes in nanorods. This phenomenon will be illustrated by theoretical calculations presented in the next Section.

Similar analysis was also conducted for nanoblock structures with larger neck widths of $w = 8.8$ and 13.2 nm. We did not find significant differences in the parameters $\Delta E$, $Q$, and $T_2$, and only a slight reduction in the resonance energy $E_c$ arising from the reduction of the total length of the chain. Insensitivity of $\Delta E$, $Q$, and $T_2$ to the neck width variations illustrates that these regions, even when their average width is only a few nanometers, do not contribute significantly to lifetime and scattering of longitudinal plasmons. Hence, radiative losses is the predominant mechanism of plasmon damping.

### 3.4. Theoretical modeling by Finite-Difference Time-Domain technique

Resonant LP scattering peaks reflect localization of the optical near-field at the nanoparticles’ surface. Field distribution and maximum enhancement factor are important for plasmonic applications. Spatial patterns of the electric field intensity may also help to identify dipolar or multipolar character of the corresponding plasmon modes. However, practical monitoring of
the near-field distribution is a difficult task [21, 22]. In these circumstances the most accessible method for gaining an insight into the near-field distribution is theoretical modeling based on numerical solution of Maxwell’s equations. This approach has proved to be accurate for metallic nanoparticles having dimensions larger than about 10 – 15 nm [1]. In this work we use Finite-Difference Time-Domain (FDTD) calculations for the modeling, which was performed using FDTD Solutions (Lumerical, Inc.) software. The idealized structures used for the modeling are similar to those shown in the schematic picture in Fig. 1. The calculations were performed on a discrete cubic mesh with spacing of 4 nm. Since width of the necks between the nanoblocks, \( w = 4.4 \text{nm} \) is close to the mesh spacing, in the regions surrounding the necks the regular mesh was overridden by a finer mesh with spacing of 2 nm. Perfectly-matched layer (PML) boundary conditions were imposed at the boundaries of the calculation domain, which was chosen large enough to avoid truncation of the field. Optical properties of gold were described using Lorentz and plasma approximations of the existing experimental data [23]. The substrate was assumed to have a refractive index of \( n = 1.77 \), close to that of sapphire. Optical extinction was determined using the Total Field-Scattered Field (TFSF) formulation. To represent the unpolarized excitation used in the experiments, two perfectly overlapping, simultaneous TFSF sources with mutually perpendicular polarizations (along the \( x \)– and \( y \)–axes) were used. FDTD calculations allow determination of extinction cross-section and electric field pattern from the same calculation. Since simulation time increases rapidly with the size of the calculation domain (or the total number of mesh points), the calculations were carried out for nanoparticles with \( N \leq 4 \) in order to maintain reasonable calculation times on a personal computer with two shared-memory processors.

Figure 4 shows the calculated extinction spectra for nanoblock and nanorod structures \((N = 4)\) together with the corresponding experimental data sets, taken from Fig. 2. The calculated data represent the spectra of extinction cross-section, \( \sigma_{\text{ext}} \), estimated from the balance of total electromagnetic power flow in and out of the TFSF region, which surrounds the nanoparticles. In Fig. 4 the measured and calculated data use different ordinate axes, whose scaling was varied to obtain close qualitative matching between these datasets (i.e., their relative scaling factor was the only adjustable parameter). As can be seen from both panels in the Figure, matching between the calculated and measured spectra is very satisfactory, especially for the nanoblock structures in Fig. 4(a). Almost all major and minor extinction features, their spectral positions (with exception of the minor extinction peaks’ positions) and relative amplitudes are reproduced by the calculations.

The minor extinction peaks assigned to the multi-polar plasmon modes in the calculated extinction spectra in Fig. 4(a) and (b) qualitatively reproduce the experimental data. Thus, in the calculated spectrum chains of nanoblocks exhibit only a weak extinction peak at the intermediate spectral position of \( E = 1.033 \text{eV} \), and a weak broad background scattering. Correspondingly, in the experimental spectrum a very weak extinction peak is most likely seen centered at the photon energy of \( E = 0.85 \text{eV} \), and rides on a low-intensity broadband background. In contrast, the calculated extinction for nanorods exhibits a much stronger intermediate peak at \( E = 1.305 \text{eV} \) and a significant spectrally broad background. In the experimental spectrum the intermediate peak is centered at the photon energy of \( E = 1.17 \text{eV} \), and a considerable broadband background extinction is present.

The existing disagreements between experiments and calculations can be explained by the differences between the idealized model used for the calculations and the conditions of the measurements. First, the average size, shape and length of nanoparticles in the fabricated ensembles may differ from those of the single nanoparticle defined in the idealized model. Second, the calculations assumed a single incidence direction parallel to the \( z \)–axis, and collection of a scattered field in the full 3D angular range of \( 4\pi \). In reality, however, both incidence and
collection directions were distributed in the conical angular range of $16 - 32^\circ$ with respect to the $z$-axis direction due to the use of infrared Cassegrainian microscope objectives. Third, our samples may have been unintentionally contaminated by dust, moisture, or other agents present in the ambient atmosphere. It is known, that deposition of dielectric layers of nanometric thickness on nanoparticles may significantly modify their plasmonic scattering spectra [24].

In order to elaborate further the distinction between dipolar and multipolar plasmon excitation, in the following we will present a brief analysis of calculated near-field intensity patterns at important spectral positions, shown in Fig. 5. The field was monitored on an $x-y$ plane located at half-height of the nanoblocks, i.e., 20 nm above the substrate. The intensity is normalized to that of the incident field, and consequently, spatial maps shown in the Figure represent the field intensity enhancement factor.

For the nanoblock sample (Fig. 5(a)), the lowest-energy extinction peak at $E = 0.44$ eV has electric field concentrated predominantly at the extreme longitudinal (top and bottom) bound-

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Fig. 4. Calculated spectra of extinction cross-section for nanoblocks (a), and nanorods (b) with $N = 4$. For comparison, the corresponding experimental spectra from Fig. 4 are also shown.
Fig. 5. Calculated near-field patterns on the $x$–$y$ plane at a half-height of the nanoparticles, (a) for nanoblock, and (b) for nanorod structures with $N = 4$.

aries of the nanoparticle, and also a significant field distribution along the extreme transverse (left and right) boundaries of the top and bottom nanoblocks. In the monitored plane this mode has a maximum field intensity enhancement factor of about 200 (even stronger enhancement can be expected at the planes coincident with the top and bottom surfaces of the nanoblocks). Although, strictly speaking, the fundamental LP resonance of the entire nanoparticle has a multipolar spatial mode, the overall longitudinal distribution of the near-field intensity pattern is predominantly dipolar. This trend can be expected to become even stronger in longer chains of nanoblocks due to the stronger overall elongation of the chain. Therefore, we can informally categorize this mode as “predominantly dipolar”. At the spectral position $E = 1.033$ eV of the minor extinction peak the near-field redistributes closer to the middle section of the chain, and
its pattern becomes quite complex, acquiring clear signatures of a multipolar LSP mode. The maximum field enhancement factor of this mode is about 70. Finally, at the peak which was previously classified as corresponding to the LP mode of a single nanoblock \( (E = 1.82 \text{ eV}) \), field patterns around each nanoblock are nearly identical. The overall LSP mode is multipolar, with numerous high-intensity spots where the enhancement factor reaches about 90.

As mentioned above, in order to roughly represent depolarized excitation conditions, FDTD simulations employed two excitation sources having linear polarizations parallel and perpendicular to the nanoparticle elongation direction. This circumstance has resulted in a slight asymmetry of the calculated field patterns with respect to the long axis of the nanorod or chain of nanoblocks. We have verified in separate calculations that selective excitation of longitudinal modes by a single source polarized parallel to the elongation axis of the nanoparticles would remove the asymmetry. For example, in chains of nanoblocks the tilted lines of high-intensity field (Fig. 5(a)) straighten out and break into several high-intensity spots localized at the narrow necks between the nanoblocks.

For the nanorod sample (Fig. 5(b)), the fundamental LP mode at \( E = 0.496 \text{ eV} \) is predominantly dipolar (due to the high aspect-ratio of the nanorod) and has enhancement factor of about 240. This pattern is retained (albeit with lower enhancement factors) with increasing photon energy till the minor extinction peak at \( E = 1.305 \text{ eV} \), when it becomes replaced by a four-peak pattern reminiscent of a standing-wave, observed previously [21]. This peak therefore represents the lowest-energy dipole-allowed multipolar mode of the nanorod. The highest-energy extinction peak at \( E = 2.07 \text{ eV} \) also has a standing-wave pattern, but with even more maxima (some asymmetry of the pattern along the \( x \)-axis is caused by the excitation source polarized along the same direction). Away from the fundamental LP peak the field enhancement factor decreases steadily.

The above analysis may help one understand the relative weakness of LP scattering in the spectral interval between the major extinction peaks of nanoblock chains (Fig. 4). Periodicity of the chain along the \( y \)-axis direction creates favorable conditions for certain LP modes only. In our case, longitudinal modes of the entire chain (low-energy) and of single nanoblocks (high-energy), are dominant. At intermediate photon energies, only those modes whose longitudinal distribution of the field intensity is commensurate with periodicity of the chain can provide a limited contribution to the optical scattering due to LSP. In contrast, smooth nanorods will not exhibit such selectivity and sustain LSP modes whose longitudinal field distribution is commensurate with the total length of the rod. Consequently, stronger resonant and broadband scattering will be seen at intermediate energies.

4. Conclusions

We have proposed and implemented elongated periodic chains of gold nanoblocks, which can sustain dipolar LP modes similar as in smooth nanorods, and simultaneously inhibit excitation of multipolar LP modes. The dipolar LP modes of chains of nanoblocks are spectrally tunable by tailoring the chain length in the IR spectral range; their damping occurs mainly due to radiative losses, and generally has a magnitude almost identical to that found in smooth nanorods of equivalent length. Hence, elongated nanoparticles possessing periodically corrugated shapes can be regarded as interesting systems for plasmonic applications that require spectrally-selective response at IR or longer wavelengths. One attractive area of such applications might be in signal receivers to be used for THz imaging in homeland security.

Acknowledgements

K.U. acknowledges support from Grant-in-Aid from Japan Science and Technology Agency (Potentiality Verification Stage). This work was supported by the KAKENHI Grants-in-Aid for
Scientific Research on Priority Area “Strong Photons-Molecules Coupling Fields (No. 470 and No. 17360110), and by Hokkaido Innovation through Nanotechnology Support (HINTS) from the Ministry of Education, Science, Sports and Culture of Japan.