Tuning resonances on crescent-shaped noble-metal nanoparticles

H Rochholz, N Bocchio and M Kreiter

Max Planck Institute for Polymer Research, D-55021 Mainz, Germany
E-mail: kreiter@mpip-mainz.mpg.de

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Abstract. The geometry of crescent-shaped noble-metal nanoparticles is systematically varied in terms of shape and size. The resulting changes in the plasmonic resonances of these structures are investigated by extinction spectroscopy revealing a rich polarization-dependent response in the near-infrared region of the electromagnetic spectrum. A first approach towards the understanding of this behaviour, in analogy to previous models on confined modes in nanometric metal slabs, is presented and discussed. Variations in several geometrical parameters lead to changes in the optical response that can be understood within this model. Qualitative changes in the response are seen at the transition of the structures from an open ‘crescent’ to a fully connected ring, pointing to a high field localization between the two tips of the structure.
1. Introduction

Metallic structures with typical dimensions of the wavelength of light and below may support optical resonances. Those are expected to lead to drastically enhanced optical near fields upon external illumination, resulting in both enhanced excitation of a local absorber and enhanced emission of a local source which is located in this region [1, 2].

This enhanced coupling to incident and outgoing light waves in nontrivial metal structures has been identified as the major contribution to the enhancement of the Raman cross-section over more than ten orders of magnitude by rough silver films [3] with immense application potential in analytical assays [4]. In a similar way, the field enhancement on tailored optical antennae can lead to nonlinear optical effects as white light generation [5, 6]. A related property of resonant metal structures with strong field localization is the high sensitivity of their spectral response to local changes in the dielectric environment, making them promising for chemical and biosensing applications [7, 8]. A general strategy to obtain maximum field enhancements would consist of combining a strong overall resonance of a structure with very small local geometric features. Following this principle, i.e., triangles with sharp corners [9]–[11], pairs of disks separated by a narrow gap [12], single spheres on a plane [13] or colloid-templated grating structures with sharp edges [14] have been fabricated.

Another property of the resonances in nontrivial metal structures that has recently attracted enormous interest is their far field response which allows for the design of a so called metamaterial with a negative mean refractive index [15, 16] with unique optical response.

We have recently demonstrated [17] that crescent-shaped metal structures can be easily prepared in a parallel fashion on large areas. These structures support strong overall resonances in the near infrared regime and are expected to provide high field localization at their tips. In addition, they are geometrically very similar to ‘split ring resonators’ which are promising candidates for the design of metamaterials.

For most near-field effects, a structure that supports specific resonances for selectable wavelengths appears highly advantageous to match absorption or emission energies of a
chromophore or simply to be compatible with the available light sources and detectors, i.e., at telecommunication wavelengths. With this motivation we studied how the resonances of the crescents evolve with changing crescent geometry. This investigation provides, in addition to the possibility of spectral resonance tuning, some physical insight into the different types of resonant modes of these structures as well as some evidence for highly localized fields for selected geometries.

The theoretical description of the optical response of nontrivial metal structures is still a challenge. Exact analytical solutions are restricted to objects with spherical symmetry \cite{[18]}–\cite{[20]} and plane multilayer systems \cite{[21]}, approximate solutions are known for the sphere-on-plane \cite{[22]}, and double sphere geometries \cite{[23]} and, most important for our study, rectangular slabs \cite{[24]}–\cite{[26]}. The description of more complex geometries as discussed here has to rely on numerical methods. Triangular structures prepared by colloidal lithography have successfully been modelled in three dimensions (3D) including the influence of the substrate \cite{[8]} but, in many cases, numerical calculations are only available in 2D \cite{[27]} and therefore represent, at best, an approximate description of the 3D case. Since the metal crescents investigated here represent an example that is very difficult to model fully as a 3D system, we chose to study a qualitative description of their response. The crescents can be continuously transformed into a rectangular slab, representing a geometrically much simpler model system that has been studied thoroughly in theory and experiment. When the metal slabs are excited by light polarized along the long axis \cite{[28, 29]}, a family of resonances is excited. They can be interpreted as standing waves along the rod, formed by a superposition of a forward and a backward propagating mode of an infinitely extended stripe. For narrow slabs only one fundamental propagating mode, analogous to the zero-order mode in dielectric waveguides is supported for a specific wavelength. This phenomenon allows for the determination of the dispersion relation of this mode by assigning the proper integer number of nodes for the observed standing wave resonances \cite{[26, 29]}.

2. Experimental

2.1. Sample preparation

Crescent-shaped noble metal particles were prepared according to a nanosphere lithographic method as described earlier in detail \cite{[17]}. Figure 1 shows a scheme of the fabrication process. In the first step, polystyrene (PS) nanospheres (Polystyrene Nanobead: NIST, Polysciences, Warrington, USA) were randomly dispersed on a clean glass substrate (Objekttraeger Glas, Menzel Glaeser, Germany) to form a sub-monolayer of spatially separated colloids. Next, gold was deposited on the colloid-covered substrate by thermal evaporation (Auto 306, Edwards, Sussex, UK). In this step, the tilt angle $\theta$ of the surface normal with respect to the metal source beam was to be adjusted as desired. In addition, the substrate was rotated about the surface normal by an azimuthal angle $\varphi$ in between evaporation steps, to adjust the opening gap between the two tips in the structure. After metal deposition, the gold-coated samples were exposed to an argon ion beam inciding perpendicular to the substrate (RR-I SQ76, Roth & Rau, Wüstenbrand, Germany), removing the gold not masked by the PS nanospheres. The PS spheres were removed from the substrate mechanically by means of an adhesive tape (Scotch Magic Tape 810 : 19 mm $\times$ 33 m, 3M France), and a second etching step was applied to the samples to remove extra sputtered material on the surface and ensure clean and clear structures.
Figure 1. Sketch of the crescent preparation process.

Figure 2. (a) Sketch of the particle geometry indicating the rotation angle $\varphi$ for double evaporation, the diameter $d_{\text{coll}}$ of the masking colloid and a coordinate system to be referred to. The angle $\alpha$ defines the circular segment ideally covered by the gold film in a single evaporation step. (b) SEM micrograph of an experimentally obtained structure in comparison with the theoretically predicted contour after double evaporation ($d_{\text{coll}} = 400$ nm, $\varphi = 120^\circ$).

Figure 2 depicts an idealized geometry of a crescent structure as obtained by double evaporation. In a single evaporation step, the obtained structure covers a circle segment corresponding to an angle $\alpha$. Following basic geometrical considerations, $\alpha$ is obtained as a function of the tilt angle $\theta$ as

$$\cos \left(180 - \frac{\alpha}{2}\right) = \frac{\tan(\theta)}{1 + \cos(\theta) + \sin(\theta) \tan(\theta)}.$$

For the $\theta = 30^\circ$ used for this study, this yields $\alpha = 211^\circ$. By double evaporation, the circular segment covered by the structure is increased by the rotation angle $\varphi$. The resulting opening angle $\gamma$ is then obtained as $\gamma = 360^\circ - \alpha - \varphi$ by choosing the appropriate $\varphi$. The maximum crescent width $'w'$ of the metal is given as

$$w = \frac{d_{\text{coll}}}{2} \left[ 1 - \frac{(1 - \sin(\theta))}{\cos(\theta)} \right].$$

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Yielding for the $\theta = 30^\circ$ used throughout the studies discussed here

\[ w = 0.42 \cdot \frac{d_{\text{coll}}}{2}. \]

The crescents diameter can be adjusted by choosing the appropriate diameter of the templating colloid. Furthermore, the film thickness is directly accessible by controlling the amount of gold deposited on the sample, with an upper limit related to the radius of the colloid.

It must be noted that in reality deviations from the idealized geometry suggested in figure 2(a) occur. Granularity, as it is commonly known for thermally evaporated metal films, is seen in the scanning electron images figure 2(b); this translates, in turn, into a not perfectly defined contour. An extra point to be considered is that also the tips are not infinitely sharp as would be the case for a perfect geometry. As additional systematic uncertainties, lateral variations in evaporated layer thickness, etching and aggregation of colloids should be taken into account.

2.2. Characterization

A commonly applied [7, 15, 28, 29] straightforward method for the investigation of local resonances is UV-Vis/NIR transmission spectroscopy. This technique provides quick and easy information since local resonances are generally accompanied by an increase both in optical absorption and scattering, which leads to an increased extinction measured experimentally. Polarized spectra of particles produced on glass substrates were recorded in a UV-Vis-NIR spectrometer equipped with polarization optics (Perkin-Elmer, Lambda 900) operating in transmission mode. Scanning electron micrographs were recorded on a Leo electron microscope, model 912.

3. Results and discussion

The system exhibits completely different extinction spectra upon illumination with light polarized parallel and perpendicular to the symmetry plane of the structures, namely, along the $x$- and $y$-axis, according to the sketch in figure 2(a). In the following, these excitation conditions will be correspondingly referred to as ‘$u$’ in the parallel case, and ‘$c$’ in the perpendicular one: the structures can be read as the letters ‘$u$’ and ‘$c$’ for these two cases if the electrical field is assumed to be vertical.

The particular polarization-dependent behaviour is exemplified in figure 3, where both the extinction for non-polarized light and for the two fundamental linear polarizations is shown. The strongest observed peaks appear exclusively for one linear polarization, thus providing a good means for their classification. The two strong maxima excited by the $c$-illumination mode are termed $c_1$ and $c_2$; the strong resonance excited in the ‘$u$’-illumination mode is termed $u_1$.

Two more, less intense maxima are visible in figure 3. Firstly, at $\lambda = 550$ nm in the $c$ illumination mode, and at $\lambda = 535$ nm in the $u$ illumination mode two maxima are seen. This wavelength range roughly matches the resonance wavelengths observed for very small gold particles, disks or rods [20, 30]; for this reason, this resonance will be termed as ‘particle plasmon’ (pp) in the following. Around 1650 nm, another resonance, is observed as a shoulder for both polarization modes and is termed as ‘$w_1$’ (w stands for ‘weak’). Below 500 nm, a gradual increase in extinction is seen; such increase is reminiscent to the increased extinction of spherical gold.
Figure 3. Extinction for light polarized parallel and perpendicular to the symmetry axis of the crescents (lower spectra), non-polarized extinction and sum of extinctions obtained for the two linear polarizations (upper spectra). The datasets are vertically offset and normalized. Colloid diameter, layer thickness and rotation angle are $d_{\text{coll}} = 150$ nm, $d_{\text{Au}} = 20 + 20$ nm and $\varphi = 120^\circ$ respectively.

Colloids and thin gold films in this wavelength range, usually attributed to the onset of intraband transitions [30].

The sum of the extinctions for linearly polarized light is in rough agreement with the experimental result obtained for non-polarized light; the difference illustrates deviations occurring due to data taken on different areas on the sample. Within experimental accuracy, the extinction $E(\delta)$ for an arbitrary angle $\delta$ of the polarization of the incident light relative to the long axis of the crescents follows

$$E(\delta) = E_U \sin^2(\delta) + E_C \cos^2(\delta).$$

with the extinctions $E_U$ and $E_C$ as obtained for u- and c-polarizations. This shows that the microscopic symmetry of the sample directly translates in a macroscopic response and no further effects due to an imperfect sample preparation or experimental artifacts are observed.

3.1. Fitting

The next step to condense the spectral information consists in fitting the data as a superposition of peaks. Figure 4(a) shows that a superposition of Lorentzian curves yields a remarkably good agreement with the experiment while a superposition of Gaussian curves does not.

This implies that even though an ensemble of crescents is investigated, the major contribution to the finite width of the measured maxima is due to the lifetime-limited line width of the resonances while any contribution due to inhomogeneous broadening is smaller than the latter. As an important consequence, the line widths as obtained from the fits are a true physical property of the observed resonances. Furthermore, it is noted that the peak around 540 nm does not fit...
Figure 4. Linear least square fit to an experimentally determined extinction (identical dataset as in figure 3, c-polarized light) as a superposition of four Lorentzian peaks (a) and four Gaussian peaks (b). The residual is shown in the lower part of the graphs where the obtained value for $\chi^2$ is indicated as well. The fit is restricted to the experimental data for $\lambda > 500$ nm.

very well. This deviation increases if more data points at smaller wavelengths are taken into account. Thus while the extinction for the longer wavelengths can be well described in terms of Lorentzian resonators, in the regime where the interband transitions are expected, an increased additional absorption mechanism is observed. In the following, all peak positions are determined from Lorentzian fits.

3.2. Crescent opening

By double evaporation, crescents with different opening angles $\varphi$ were prepared and the response of the extinction spectrum was studied. The results are shown in figure 5. We first note that the spectra obtained for c-polarization show a continuous evolution of the peak positions for $0^\circ \leq \varphi \leq 120^\circ$ which corresponds to structures with a large gap between the two tips of the structure. The response obtained for $\varphi = 140^\circ$, where for perfect samples a very small gap is expected and for $\varphi = 160^\circ$ corresponding to a metal connection across the gap are similar but do not fit in the continuous evolution of the structures with large gap. For the symmetric structure obtained for $\varphi = 180^\circ$, again a qualitatively different behaviour is observed. We now first concentrate on the 'large gap' case ($0^\circ \leq \varphi \leq 120^\circ$). The resonance peaks c1, w1, u1, c1 and pp are assigned based on the dataset corresponding to $\varphi = 120^\circ$ (compare figure 3). An additional, long-wavelength resonance, ‘w0’, is weakly visible at higher wavelengths for $\varphi = 0^\circ$.

The strength of w0 is highly variable between preparations. We would like to discuss some heuristic observations that were made regarding w0 before moving on with the interpretation of the spectra. In figure 6, extinction spectra are compared for structures where 40 nm gold were deposited in a single process and for structures where the same amount of gold was deposited in two subsequent evaporations (20 nm each). In between the two evaporations, the vacuum chamber was opened shortly, thus exposing the sample to ambient air. Some minor change in resonance wavelength of c1, u1, c2 and pp are seen, being most pronounced for c1. Still, the relative strength of these resonances is quite reproducible. For w0, the situation is drastically
Figure 5. Extinction spectra for varying crescent opening, produced by double evaporation before and after rotation by \( \varphi \), as indicated in figure 1. The diameter of the masking colloid and the film thickness were held constant at \( d_{\text{coll}} = 150 \text{ nm} \) and \( d_{\text{Au}} = 2 \times 20 \text{ nm} \) respectively. (a)–(c) shows the extinction spectra recorded with \( u \)-polarized, \( c \)-polarized and non-polarized light, respectively. In (b) the contour as it would be obtained for a perfect preparation process is sketched for each value of \( \varphi \).

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Different: while being of significant strength for structures prepared in a single evaporation step, this resonance is only very weakly visible when nominally identical structures are prepared in two subsequent evaporations. The structures with \( \varphi > 0 \) were all prepared in two evaporation steps. The resulting strength of \( w_0 \) is quite variable as can be seen in figure 5. We note furthermore that the strength of \( w_1 \) appears to be correlated with the one of \( w_0 \). This may suggest that \( w_0 \) and \( w_1 \) are based on a physical effect that is somewhat different from the effect leading to the other, stronger maxima, probably, colloid aggregation and the resulting optical interaction of crescents plays some role for these features. In the following, the discussion will be focused on the strong, reproducibly observed features.

For all resonance peaks except the one around 550 nm, a clear red shift with increasing \( \varphi \) (decreasing opening angle \( \gamma \)) is observed up to \( \varphi = 120^\circ \). For the ‘small gap’-structures obtained at higher \( \varphi \), the spectrum obtained with \( c \)-polarization changes qualitatively. A new double peak...
Figure 6. Unpolarized extinction spectra for crescents obtained by a single evaporation of 40 nm gold and by evaporating two times 20 nm ($d_{\text{coll}} = 150$, $\varphi = 0^\circ$).

Figure 7. Representative scanning electron micrographs of crescents prepared with $\varphi = 140^\circ$ ($d_{\text{coll}} = 150$ nm, $d_{\text{Au}} = 20$ nm + 20 nm).

structure emerges around 1070 nm and a peak appears around 1900 nm, which does not fit in the progression of the increasingly red-shifted ‘c’ peaks. This behaviour can be interpreted as being due to the two tips starting to interact optically at $\varphi = 140^\circ$, although for a perfect geometry a remaining gap angle of $\gamma = 9^\circ$ is anticipated.

In figure 7, a scanning electron micrograph of such structures is shown. The majority of the crescents still appear to have a small open gap but apparently sufficiently close tips already interact, dominating the optical response of the entire structure. No effect of gap closing is seen in the extinction spectra for $\mathbf{u}$-illumination. This can be understood based on the symmetry of both illumination conditions and the crescents. Upon illumination with $\mathbf{u}$-polarized light the tips...
Figure 8. (a) UV-Vis extinction for non-polarized, c- and u-polarized light of a structure that was obtained by a triple evaporation routine with $\varphi$: 0°, 120°, 240°, $d_{\text{Au}} = 3 \times 20$ nm, $d_{\text{coll}} = 150$ nm colloids; (b) sketch of the structure as produced and of the proposed oscillating charge distribution of the resonance; (c) corresponding scanning electron micrograph.

of the structure are equally charged at any time and at the gap no current flows. As a result, no drastic effect on the resonances is observed and the spectra for $\varphi = 160°$ are very similar to the ones obtained for $\varphi = 140°$. Scanning electron micrographs of these two samples show in both cases a majority of ring-like structures that still exhibit a small gap. It has been shown experimentally [12] that the opening of a small gap between metal disks leads to a drastic change in their optical response which is very similar to our observations. For the case of a pair of metal spheres, a theoretical investigation [31] on the transition from separated to connected case showed a singularity when the spheres touch, different types of modes arise for these two cases. While this analogy to existing study give a qualitative idea for the effects observed here, a quantitative understanding of the resonances on structures with small gaps requires an understanding of the mutual interaction of the tips of the structure which would require detailed numerical studies.

For $\varphi = 180°$ closed structures with two symmetry planes are obtained. They exhibit an optical response which is again qualitatively different from the ‘almost connected’ ring structures obtained with $\varphi = 160°$ and $\varphi = 140°$. Only one characteristic resonance peak for each polarization is observed at 1419 nm for u and at 1377 nm for c-polarizations, which resembles the response of ring-like structures [32]. The fact that both resonances do not appear at the same wavelengths when excited in either the c or u conditions reflects the fact that by double evaporation still no rotational symmetry is obtained. An extra shoulder is observed in the 800 nm range for the u-polarization measurement performed on this sample.

Structures that almost exhibit rotational symmetry are obtained when three metal layers are deposited on top of the colloidal mask with equal angular spacing in between deposition steps ($\varphi$: 0°, 120°, 240°). Extinction spectra measured on such structures for the two main polarizations and for non-polarized light are shown in figure 8. Here, the results for two orthogonal polarizations
are almost equivalent, as might be expected from the symmetry of the particles. From this we can conclude that this resonance must be identified with the dipolar resonance on ring-shaped metal objects as discussed by Aizpurua et al [32] with a charge distribution as sketched in figure 8(c).

3.3. Interpretation

Peak positions as determined from fitting Lorentzian curves to the experimental data for structures with large gaps \((\varphi \leq 120^\circ)\) are displayed in figure 9(a). Apart from the \(pp\) resonance, all maxima appear clearly red shifted with increasing rotation angles \((\varphi)\) in between deposition steps. This can be understood in analogy to the multipolar resonances on a rectangular slab [29]. In this case, the resonances are assigned to a superposition of forward and backward propagating modes supported by the gold slab. A resonance occurs whenever the resonance condition

\[
\frac{n\lambda_s}{2} = L,
\]

is fulfilled, \(n\) being the order of the resonance, \(L\) the length of the supporting metal structure and \(\lambda_s\) the wavelength of the supported mode. Although the crescents under investigation are clearly different from a rectangular slab since they are both bent and do not possess a constant width of the metal, comparison of these two cases provides first physical understanding of the resonances. First evidence that the description as slabs even provides quantitative information is rationalized by normalizing the experimentally observed resonance wavelengths by the contour length \(l_c\) of a crescent, approximated by

\[
l_c = \frac{d_{\text{coll}}}{2}(\alpha + \varphi),
\]

where \(d_{\text{coll}}\) represents the diameter of the mask, \(\alpha\) and \(\varphi\) are geometrical parameters, as depicted in figure 2. This quantity is identified with the length \(L\) of the model slab. If the dispersion relation \(\omega(k)\) for the guided modes is linear in the frequency regime under consideration, the
Figure 10. Sketch of charge distribution for the resonance on a closed ring and the three strongest resonances of open crescents.

quantity $\lambda_{res}/l_c$ is expected to be constant. A detailed plot of this quantity for the measured resonances is shown in figure 9(b). An approximately constant value for $\lambda_{res}/l_c$ is seen for the $u_1$ and $c_1$ resonances, while the short-wavelength resonance $c_2$ shows a slight deviation from this behaviour. The resonances at $\varphi = 140^\circ$ and beyond are not considered since here gap closing, a clear topological change occurs. The $pp$ resonance is included for comparison. Its resonance wavelength is fairly independent of $\varphi$; as a consequence, the quantity $\lambda_{res}/l_c$ exhibits a clear and regular decrease, according to the increase in the particles contour length.

A dispersion plot can be constructed calculating the wavevector $k$ and the angular frequency $\omega$, as follows

$$k = \frac{2\pi}{\lambda} = \frac{n\pi}{l_c} = \frac{n\pi}{[d_{coll}/2(\varphi + \alpha)]} = \frac{2n\pi}{d_{coll}(\varphi + \alpha)},$$
$$\omega = 2\pi \nu = 2\pi \frac{c}{\lambda_{res}}.$$

The order $n$ of the resonances can be deduced from the observation that $u_1$ is continuously transformed into the dipolar ring resonance upon gap closure. Thus $u_1$ is identified with the charge distribution corresponding to $n = 2$ as sketched in figure 10. Then, $c_1$ and $c_2$ can be assigned to $n = 1$ and $n = 3$, respectively. In order to excite these resonances, the electrical field vector must be parallel to the net polarization of the crescents in perfect agreement with the experimental observation.

Using these values for $n$, the dispersion curve shown in figure 11 is constructed. The behaviour of $c_1$ ($n = 1$), $u_1$ ($n = 2$) and $c_2$ ($n = 3$) is in good agreement with a dispersion curve as it was discussed for the rectangular slab [29], thus providing a very good description of the three strongest resonances. The weaker $w_0$ and $w_1$ resonances cannot be described in this simple picture. We note that they would follow the same dispersion curve if the non-integer orders $n_{(w_0)} = 0.65$ and $n_{(w_1)} = 1.3$ were assigned; remarkably these numbers differ by a factor of two. In this context, more complex resonances on metal slabs [24, 25] could play a role as well as effects due to the deviation of the crescent shape from this highly simplified first approach. While the slab model applied fails to describe the $pp$ resonance, a simple interpretation will be given based on the experimental data discussed below.

Note that the description in terms of standing waves on a slab with two no interacting ends is restricted to large-gap geometries ($0^\circ \leq \varphi \leq 120^\circ$), it is neither applicable for the ‘small gap’ ($140^\circ \leq \varphi \leq 160^\circ$) nor for the fully symmetric structures ($\varphi = 180^\circ$).
Figure 11. Dispersion plot $\omega(k)$ for five resonances. The light line in the glass substrate (red) and in air (black) are indicated. The dotted line indicates the limiting frequency for surface plasmons on plane substrates.

Figure 12. (a) Extinction spectra of crescents with varying metal thickness with otherwise unchanged geometry, peak position versus gold thickness. (b) The colloid diameter was held constant at $d_{\text{coll}} = 150$ nm, only a single evaporation step was used ($\varphi = 0^\circ$).

3.4. Crescent thickness

The influence of the variations in the thickness of the gold film is investigated next. Figure 12 shows a set of experiments where the nominal gold thickness $d_{\text{Au}}$ was varied from 20 to 45 nm and extinction was measured with non-polarized light. Three maxima in the near infrared region ($w_0$, $c_1$, $u_1$) as well as the $pp$ peak at 520 nm are clearly visible. While no change in the $pp$ peak is seen, the other resonances shift to smaller wavelengths as the film thickness is increased. This shift, which appears substantial when the film has 20 or 30 nm in thickness, becomes rather small when the thickness is further increased. This shows that small thickness variations are not
Figure 13. (a) Extinction spectra for different choices of diameter of the masking colloid $d_{\text{coll}}$. The spectra for $d_{\text{coll}} = 60 \text{ nm}$, $d_{\text{coll}} = 80 \text{ nm}$ and $d_{\text{coll}} = 100 \text{ nm}$ are multiplied by a factor ten for better visibility. A gold thickness of $d_{\text{Au}} = 20 \text{ nm}$ in a single evaporation ($\phi = 0^\circ$) was used for all samples. The measurements were performed with non-polarized light. (b) Peak positions as a function of colloid diameter. (c) Peak wavelength normalized by $l_c$.

critical in the latter thickness regime, at least, for the shorter wavelength resonances. From an experimental point of view, the selected particle size sets an upper limit to the maximum possible achievable thickness; the selection of bigger colloids as masks would allow for further study in this direction.

The observed variations may be explained by the granularity of evaporated films which leads to a reduced conductance for thicknesses below $d_{\text{Au}} = 20 \text{ nm}$, resulting in a different effective optical response of the metal layer. Again, the strength of the $w0$ resonance shows large variations between different preparations.

3.5. Crescent diameter

Extinction spectra of crescents with varying diameter are presented in figure 13(a). Although the signal for small $d_{\text{coll}}$ is weak due to both a reduced extinction cross-section of the individual objects and a low particle density on the surface, maxima can be determined down to
$d_{\text{coll}} = 60 \text{ nm}$. The maximum positions as determined from a fit are displayed in figure 13(b). As an empirical trend, a linear dependency of the peak wavelength on crescent diameter is observed; the data appear to lie close to lines that intersect for decreasing crescent diameters approximately at the pp wavelength (530 nm). In this case it is not possible to collapse the resonance frequencies as obtained from crescents with varying diameter on the same dispersion curve. This can be understood since upon increasing $d_{\text{coll}}$, both the contour length $l_c$ and the width $w$ of the crescent are increased while variations in $\varphi$ only change $l_c$ while keeping a constant crescent width. Normalization by the contour length (figure 13(c)) suggests a decrease in the wavelength of guided modes with increasing width $w$ of the structures.

Furthermore, an apparent shift of the pp resonance to longer wavelengths is noted for increasing crescent’s diameters in the size range explored, the shift being more pronounced for u than for c-polarization. This is most clearly seen for the largest masks ($d_{\text{coll}} = 300 \text{ nm}$, $d_{\text{coll}} = 400 \text{ nm}$); the corresponding extinction curves are displayed in figure 14. This observation points towards an interpretation for these maxima. Locally, the crescents behave similar to a rod that supports, in addition to the standing waves along its long axis, resonances along its short axis. Such resonances are excited on the crescents for u- and c-polarizations predominantly at the positions indicated in figure 14(c). As a consequence, u light excitation corresponds to resonances

**Figure 14.** (a) and (b) pp resonance for $d_{\text{coll}} = 400 \text{ nm}$ and $d_{\text{coll}} = 300 \text{ nm}$ as in figure 13. (c) Sketch of the polarization of a resonance which is perpendicular to the rod for the two fundamental polarizations.
on a broader rod than c-light excitation, explaining the observed red shift (compare [33]). Upon excitation with c light only a weak maximum is present in agreement with the observation that in this case the $\varphi = 0^\circ$ crescent does not exhibit much portions where transverse resonances can be excited. A reinvestigation of the effect of a variable $\varphi$ (figure 5) shows that the strength of pp in c-polarized extinction increases for increasing $\varphi$. This is intuitively clear since for a more closed structure a longer portion can be described as a rod oriented perpendicular to the exciting electrical field in e-polarization.

3.6. Summary

The optical resonances supported by crescent-shaped metal nanostructures as prepared by colloidal lithography were investigated by UV/VIS-NIR extinction spectroscopy. Size, film thickness, opening and metal deposition angles of the structures were varied and the influence of these parameters on the observed resonances was investigated experimentally. It could be shown that the stronger resonances are exclusively excited by light with a linear polarization either parallel or perpendicular to the symmetry axis of the structure. Lorentzian curves are very well suited for a quantitative description of the observed response, suggesting that the measured line widths are lifetime-limited.

Significant shifts in resonance position are observed when the size or the opening angle of the structures is varied, allowing for a fine tuning of specific resonances in a desired wavelength range. For the most prominent resonances, the response to a change in the crescent’s contour length can be approximately described in terms of standing waves along the structure formed by the fundamental and higher-order propagating modes along a metal stripe as long as interaction between the tips of the structure can be neglected. Fundamentally different responses are seen for crescents that have clearly separated tips, tips separated by only a small gap and overlapping tips. This may point to high field enhancement effects for structures with a small gap. One additional peak in the visible range is identified as the transverse resonance of a rod while two more weak resonances are visible which are not fully understood and are highly sensitive to preparation conditions. The main resonances change upon variations in metal layer thickness and diameter of the masking colloid in a way that is in qualitative agreement with this interpretation. We expect that a full 3D theoretical model of the observed response would help to gain more insight, especially into the nature of the weaker resonances, but this type of calculation is still a theoretical challenge.

From an experimental point of view, the high tunability of the optical response of this type of nanostructure as it was explored, along with the ease of fabrication and the possibility to generate structures with two strongly interacting tips, makes the crescent-shaped particles a promising system for all applications related to near field enhancement.

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