# Description of scientific work

*1. First and last name*

> Tomasz Jan Antosiewicz

*2. Held diplomas, titles, and degrees*

> a) MSc cum laude, physics – Faculty of Physics, University of Warsaw, 14.06.2005, English title: *Propagation of electromagnetic waves through a dielectric medium with embedded nanowires* (original title in Polish: *Propagacja fali elektromagnetycznej w układzie nanodrutów zanurzonych w dielektryku).*

> b) PhD cum laude, physics – Faculty of Physics, University of Warsaw, 14.12.2009, English title: *Impact of metalized probe nanostructure on the resolution of scanning near-field optical microscopes* (original title in Polish: *Wpływ nanostruktury sondy metalizowanej na rozdzielczość optycznego mikroskopu skaningowego bliskiego pola).*

*3. Employment at scientific institutions*

> a) University of Warsaw, Interdisciplinary Centre for Mathematical and Computational Modeling, 08.02.2010-31.12.2010, position: adjunct (adiunkt naukowy)

> b) Chalmers University of Technology, Department of Applied Physics, 01.01.2011-30.06.2013, post-doctoral research fellowship (including 6 month of parental leave)

> c) University of Warsaw, Centre of New Technologies, since 01.07.2013, position: adjunct (adiunkt naukowy)

*4. Scientific contribution:*

*a) title of scientific contribution:*

> **Absorption of light in plasmonic nanostructures**

*b) publications forming the core of the scientific contribution:*

> 1. Carl Wadell*, **Tomasz J. Antosiewicz***, Christoph Langhammer (* equal contribution), Optical absorption engineering in stacked plasmonic Au-SiO2-Pd nanoantennas, Nano Lett. 12, 4784-4790 (2012).
> 2. **Tomasz J. Antosiewicz**, S. Peter Apell, Carl Wadell, Christoph Langhammer, Absorption enhancement in lossy transition metal elements of plasmonic nanosandwitches, J. Phys. Chem C 116, 20522-20529 (2012).
> 3. **Tomasz J. Antosiewicz**, S. Peter Apell, Optical enhancement of plasmonic activity of catalytic metal nanoparticles, RSC Adv. 5, 6378-6384 (2015).

4. **Tomasz J. Antosiewicz**, Carl Wadell, Christoph Langhammer, Plasmon-assisted indirect light absorption engineering in small transition metal catalyst nanoparticles, Adv. Opt. Mater. 3, 1591-1599 (2015).
5. **Tomasz J. Antosiewicz**, S. Peter Apell, Timur Shegai, Plasmon-exciton interactions in a core-shell geometry: From enhanced absorption to strong coupling, ACS Photonics 1, 454-463 (2014).
6. **Tomasz J. Antosiewicz**, S. Peter Apell, Michael Zäch, Igor Zorić, Christoph Langhammer, Oscillatory optical response of an amorphous two-dimensional array of gold nanoparticles, Phys. Rev. Lett. 109, 247401 (2012).
7. **Tomasz J. Antosiewicz**, S. Peter Apell, Plasmonic glasses: Optical properties of amorphous metal-dielectric composites, Opt. Express, 22, 2031-2042 (2014).
8. **Tomasz J. Antosiewicz**, Tomasz Tarkowski, Localized surface plasmon decay pathways in disordered two-dimensional nanoparticle arrays, ACS Photonics 2, 1732-1738 (2015).

*c) description of goal and results of scientific contribution:*

The main objective set forth was a detailed study of light absorption in single metallic nanostructures which support localized surface plasmon resonances and arranged in amorphous (with short range order) one-, two- and three-dimensional arrays. This research line was motivated by:

1) A need to fill in gaps in the knowledge on absorptive properties of plasmonic nanostructures.
2) To show that absorption in plasmonic nanostructures is not a parasitic property, but is rather an undervalued property with interesting physics and potential real-world applications.
3) To tackle a general question of the correct approach to maximize absorption in matter under the assumption of using only a finite amount of material.

The complexity of the considered question necessitated that two main research avenues were pursued. The first aspect was a study of absorptive properties of single nanostructures with an internal ordering that determined absorption. The second aspect of this work involved elucidating how mutual coupling between nanostructures arranged in arrays affected their optical properties, paying special interest to their absorptive properties.

The scientific contribution contained within the eight above listed papers begins with work **1**, whose aim is to introduce a nanoplasmonic system consisting of two resonators with the goal of enhancing light absorption. The envisioned mechanism makes use of an optical antenna (one of the resonators) to collect incident light (e.g. solar radiation) and direct it to the second resonator to be absorbed. The paper **2** presents this concept in a broader context of electromagnetic coupling between a resonator made of a good plasmonic metal (noble metal) and another transition metal with large losses. Within this work the impact of this mutual coupling on absorption is investigated. Work **3** focuses on how the material properties of transition metals affect obtainable absorption enhancement values and discusses maximization of absorption enhancement in light of extinction sum rules. Paper **4** summarizes the conclusions of the preceding works and based on their message proposes an antenna-catalytic reactor nanostructure for very efficient light absorption. Work **5** discusses absorption in plasmon-exciton nanosystems and the role absorption measurements play in determining the structure's optical properties. The last three papers **6-8** form a series of works in which a model describing the optical properties of amorphous arrays on plasmonic nanostructures is developed, its predictions confronted with experimental measurements and explicit numerical calculations. The first of these works, paper **6**,

describes the model for a two-dimensional amorphous array. Paper **7** builds upon the previous work and extends the model to both one- and three-dimensional systems and to arbitrary polarization and incidence angles. It also discusses briefly the impact of the interactions within such arrays on scattering and absorption, a subject that is developed in depth in paper **8**.

*Introduction*

Strong interaction of light with metallic nanoparticles is made possible by the presence of conduction electrons. A good qualitative description of the phenomenon refers to a coherent and collective movement of conduction electrons when the particles are illuminated by light. This movement induces the appearance of charges at opposite ends of the nanoparticle and the appearance of a restorative force. This allows for the existence of a resonance, whose frequency is determined by the size of the system in question, its geometry and the material properties of the resonator and its surroundings. The resonance, known as the localized surface plasmon resonance, causes the electric field to build up in the particle and at its surface and, as a consequence, a significant increase of its optical cross sections in comparison to its geometrical cross section. In the case of particles much smaller than the wavelength a good approximation is that the field generated by the resonator is dipolar, whose near-field components are responsible for the aforementioned enhancement. It must be of course said that a finite size as well as any deviations from a spherical shape prevent the fields from matching those of an ideal dipole and any local nanosized cavities or sharp corners locally amplify the field further. However, as the particle size increases the dipolar mode ceases to be the only available mode and higher order ones become available.

From a mathematical point of view it is easy to demonstrate the existence of a dipolar resonance for a spherical particle in the quasistatic approximation [Maier, 2007]. In such a case the i-th component of the polarizability tensor $\alpha_i$ of a (in general) ellipsoidal particle with semiaxes $a$, $b$, and $c$ is expressed as

$$\alpha_i = \frac{4}{3}\pi abc\, \frac{\varepsilon - \varepsilon_m}{\varepsilon_m + L_i(\varepsilon - \varepsilon_m)},\tag{1}$$

where $\varepsilon_m$ is the permittivity of the surrounding medium, $\varepsilon$ is a complex polarizability of the particle, and $L_i$ is a geometrical factor which modifies the depolarization field and $\Sigma L_i = 1$. For spheres all three $L_i$ values are equal to 1/3 and equation (1) is simplified to the Clausius-Mossotti relations [Bohren, 2004; Moroz, 2009]. For a sphere the polarizability achieves resonance when the denominator (now equal $|\varepsilon + 2\varepsilon_m|$) assumes the minimum value. For a small or slowly varying imaginary part of the metal permittivity this occurs when $Re[\varepsilon(\omega)] = -2\varepsilon_m$. This condition, known as the Fröhlich condition, determines the frequency of the localized surface plasmon resonance of a sphere. For a sphere made of a metal described by the Drude permittivity model the resonance frequency in air is $\omega_p/\sqrt{3}$, where $\omega_p$ is the plasma frequency of the metal. Despite the fact that the permittivity of real metals deviates from a Drude function, the Fröhlich condition provides useful guidelines as to where one can expect a plasmon resonance to show up. For noble metals this resonance frequency falls typically in the visible, however, other metals with high plasma frequencies such as Al, Ga, or Tl may exhibit plasmon resonances in the ultraviolet [McMahon, 2013].

For particle comparable to the wavelength the quasistatic approximation needs to be abandoned to properly describe the spectral evolution of the plasmon resonance. The important new contributions to the optical properties come from dynamic depolarization (proportional to $k^2$, where $k$ is the

wavenumber) and dipolar radiation (proportional to $k^3$) [Moroz, 2009]. These corrections, what are introduced in equation (1), bear the name of the modified long wavelength approximation

$$\alpha_{MW} = \frac{\alpha}{1 - \frac{k^2}{a}\alpha - i\frac{2k^3}{3}\alpha} \tag{2}$$

and explain the redshift of the resonance with particle size. When considering even larger particle for which this approximation fails, it becomes necessary to use full wave description such as Mie theory, which properly predicts also the appearance of higher order modes in addition to the red shifted dipolar one [Bohren, 2004].

A localized surface plasmon resonance is damped by two mechanisms – absorption and scattering. Employing the quasistatic approximation from equation (1), the optical cross section for these two magnitudes are expressed as:

$$C_{abs} = k\,Im[\alpha], \tag{3}$$

$$C_{sca} = \frac{k^4}{6\pi}|\alpha|^2. \tag{4}$$

Due to the fact that the polarizability of a particle is proportional to its volume $V$, it is apparent that absorption scales as $V$, while scattering as $V^2$. Hence, the basic optical properties of nanoparticles are tied to their size and are indirectly dependent on the frequency range of the resonance, whose location is determined by metal and surrounding environment. The consequence of this is that the domination damping mechanism is mainly fixed for given spectral regions. Thus, for typical plasmonic metals particles with resonances in the red and longer wavelengths typically scatter light, while for resonances in the blue and shorter wavelengths particles mainly absorb. A more general statement is that the more to the red the resonance is, the larger scattering becomes, however, this depends on many factors which decide on the spectral position of the resonance in relation of the plasma frequency of the conductive material.

A localized surface plasmon resonance is accompanied by a strongly amplified electric field in the particle's vicinity. This local field can exceed the amplitude of the incident field by up to three orders of magnitude. The exact value of this enhancement depends on the particular geometry in question, sizes and materials. Regardless of the origin of this enhancement the amplified electric field results in enhanced processes which are co-localized with the enhanced fields and whose properties depend of the amplitude. Typical processes which obey these rules are fluorescence enhancement, enhancement of spontaneous emission, surface enhanced Raman scattering [Li, 2015], as well absorption enhancement in semiconductors and nonlinear processes (frequency conversion, optical signal modulation, solitons) [Kauranen, 2012].

Efficient coupling of plasmons to the above listed processes requires that the spatial overlap between the active material and the enhanced fields be as large as possible. When considering single-molecule effects such as fluorescence or Raman scattering it is important to place the molecules in hot-spots, where the local density of states is much larger than in free space. In the case of continuous materials which occupy considerable volumes it becomes necessary to fill the plasmon mode volume with the active material. Regardless of which of the two approaches in valid, the common factor in both is that it is necessary to maximize the energy of the plasmon outside the metal resonator, hence, to maximize scattering, which, of course, depends on the polarizability. However, ever present absorption in the metal is in this case a parasitic effect and decreases the overall efficiency of the processes. In certain cases the impact of absorption in metal is so strong, that it becomes impossible to increase efficiency by plasmonic

effects. Such problems were reported e.g. for semiconducting solar cells [Spinelli, 2012]. Absorption is also the reason why plasmonic waveguides are not yet broadly utilized, despite offering extreme subwavelength confinement of the signal into mode cross sections on the order of $\lambda^2/50$. The dominant reasons are considerable losses and short propagation distances, e.g. with very good waveguides achieving only 40 microns propagation length at telecommunication wavelength [Fedyanin, 2016].

Contrary to the above arguments, absorption in plasmonic nanoparticles must not necessarily be a parasitic effect. In recent years a number potential applications has been shown to be insensitive to absorption or, recently, to potentially benefit from absorption. For example, localized surface plasmon resonance biosensors, which report the presence of an analyte by a red shift of their resonance, are not affected in a significant manner by losses, as long as a plasmon peak can be identified. A natural use for plasmonic materials is in thin absorbers due to their large optical cross sections. When combined with metallic mirror substrates and appropriate spacer layers it is possible to achieve absorption close to unity [Liu, 2010; Hagglund, 2016]. In the simplest case the energy of the absorbed plasmon is converted into heat and lost. However, before heat is generated, plasmon absorption leads to the generation of hot carriers which are not in thermal equilibrium with the ionic background [Wellstood, 1994]. Before the electrons thermalize, they may instead be used to do actual work, such as current generation or to run a catalytic reaction [Mukherjee, 2013]. However, regardless of their utilization, it is important to assure efficient generation of these hot electrons. This is achieved by increasing absorption, what is the topic of this scientific contribution.

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*Absorptive properties of plasmonic nanostructures*

Publications **1** and **2** provide, respectively, an experimental and a theoretical introduction to the topic of absorption enhancement in complex plasmonic nanostructures. The simplest such structures consist of two independent resonators, typically placed in close proximity to each other. When made from low loss noble metals, the resonators exhibit narrow resonances which can interact with one another leading to mode hybridization [Prodan, 2003]. Limiting ourselves for the sake of simplicity to only dipolar resonances, hybridization yields two new modes at frequencies different from those of the original resonances. The high energy mode is one in which the two dipoles in each resonator oscillate in-phase, while for the lower energy mode the oscillation is out-of-phase and qualitatively resembles the profile of a quadrupolar resonance. Research into such coupled structures composed of either two parallel nanowires or nanodisks had been carried out before [Lagarkov, 1996] and focused on such aspects as negative magnetic permeability [Shalaev, 2005] or magnetic field enhancement [Pakizeh, 2008].

Paper **1** contains an experimental investigation of sandwich-type structures based on nanodisk pairs separated by a dielectric layer of variable thickness. The bottom disk was made from a noble metal – here gold – while the top disk is a catalytic transition metal – palladium. The measured and calculated optical absorption and scattering cross section of the structure are consistent, what allows one to relate conclusions obtained by analyzing numerical data to the experimental structures. It was observed, that absorption in palladium in the nanostructure exceeds in a wide spectrum absorption in an identical but lone Pd nanodisk and that the average enhancement exceeds two. Mode analysis yielded the induced resonances – the dominant mode is the dipolar mode of the gold disk and at resonance the phase shift between the two resonators is a function of their separation. It changes from zero (for touching disks) to almost $2\pi/3$ (for 30 nm $SiO_2$), what indicates that the Pd disk is mostly polarized by the near field generated by the induced dipolar mode of the Au disk, rather than by the incident field.

Paper **2** expands significantly the theoretical analysis of electromagnetic coupling in such nanostructures. As reference a gold-gold dimer is used which is compared to the studied Au-Pd system for a wide range of geometrical parameters. In contrast to a classical Au-Au nanostructure, the Au-Pd system does not exhibit an avoided crossing of the coupled modes both in scattering and absorption. In fact, only one resonance is observed whose characteristics are determined by the relative sizes of the Au and Pd disks. For intermediate sizes, here on the order of 70 nm in radius, scattering exhibits a clear minimum while absorption a maximum. The dominant part of this absorption occurs in Pd. When compared to a reference Pd disk, maximum enhancement reaches one order of magnitude. Using the solar spectrum as a source, total absorption in Pd disks reaches maximum values for small Pd disks placed in close proximity to the Au disk. This enhancement is made possible by efficient coupling of extra energy of the incident wave into the Pd nanoparticle by the Au disk which acts like an optical antenna. This description is augmented by a reformulation of the electromagnetic equations describing the coupled dipoles into a coupled harmonic oscillator formalism, what clearly shows the aforementioned energy transfer.

In paper **3** the focus expands to include other transition metals in order to assess how their optical properties (i.e. permittivities) affect absorption and, in general, to relate the permittivities with absorption enhancement. Metals with significantly different permittivities were chosen: ruthenium, rhodium, platinum, and vanadium – as absorbers, while silver was chosen to make the low-loss optical antenna. It was shown, that for those chosen absorbing materials the imaginary part of their permittivity, $Im(\varepsilon)$, at the optical antenna's resonance is the significant parameter affecting absorption enhancement. Of the chosen materials Ru possesses the largest value of $Im(\varepsilon)$ and offers the largest absorption enhancement which exceeds one order of magnitude, although the exact value depends on the absorber's size. Rh, Pt, and V offer respectively decreasing absorption enhancement values, in agreement with the previous conclusion. Moreover, in all cases absorption enhancement is the greatest when the absorber is a small particle placed next to the optical antenna. In this situation this small amount of absorber (which does not exhibit a significant optical resonance) is polarized by a strong near-field of the optical antenna. However, an absorption maximum can be also identified when the absorber is placed at a distance from the silver antenna. For each antenna-absorber separation an optimum absorber dimension is found which depends on the size of the optical antenna and optimum coupling conditions between the disks. Due to the fact that, in general, a material's permittivity can be decomposed into a Drude and a number of Lorentz terms, an analysis of absorption enhancement in Drude and Drude-Lorentz materials was carried out. The main factor affecting absorption enhancement is the Drude part, while the Lorentz term becomes important only when there is spectral overlap between it and the plasmon resonance of the optical antenna.

The work presented in paper **4** is founded on one of the conclusions of the previous paper, namely that maximum absorption is obtained for small particles. Due to the overreaching intent of developing a plasmonic catalytic reactor it was decided to use palladium nanoparticles of size similar to what could be fabricated. The Pd particle sized were quantified by TEM images and a median particle size was chosen – a nanodisk 3 nm thick and 4 nm in diameter. The studied system consisted of a planar substrate with a silver optical antenna covered by a protective spacer of 5 nm. It was discovered that absorption enhancement increases with an increase of the refractive index of the spacer, what is the result of drawing more energy out of the substrate. A material with a larger refractive index on top of the silver disk increases the local optical density of states in volumes occupied by absorbers. The surface of the spacer was decorated by a varying number of Pd particles, from one to full coverage, to assess the impact of stochastic properties of particle placement. In general, the expected dependence of increasing absorption with the number of particles was confirmed, although the increase was slower than linear. However, an unexpected observation was that initially increasing the number of Pd particles leads to a ca. 10% increase in absorption per particle. This can be understood in terms of the Pd particles providing an additional effective refractive index material above the substrate leading to an additional increase of the local density of states and an additional shift of the plasmon resonance to better overlap with the solar maximum, which is used as the absorption enhancement baseline (weighting function). The theoretically determined absorption enhancement was verified experimentally and depending on the size of the optical antenna it can reach 30. Follow-up work in which this absorption increase is shown to increase catalytic reaction rates is, unfortunately yet incomplete, however, a recent publication of a competing group shows that the presented concept of a plasmon enhanced antenna-reactor system is valid [Zhang, 2016].

The research described in paper **4** is important not only for basic, but also applied research, as it solves a problem of sub-10 nm catalytic particles being unable to utilize plasmonic enhancement under solar illumination. This is based on the fact that their plasmon resonances are located far in the UV, outside the solar spectrum. Utilization of coupling between an optical antenna and the absorbing catalytic nanoparticles shifts the absorber's resonance into the solar maximum. These can then be used as environment-friendly catalytic devices with enhanced reaction rates thanks to e.g. lowering of working temperatures [Christopher, 2011]. The proposed mechanism can, of course, be also used to match the optical antenna's resonance to the activation energy of a particular reaction, which is mismatched with respect to the plasmon resonance of a given nanoparticle.

Paper **5** describes electromagnetic coupling within a plasmon-exciton system, in which a plasmonic resonance of a metallic antenna interacts with an absorption line of another material. This interaction can lead to weak coupling, as well as strong coupling and Fano resonances. Due to difficulties in performing single-nanoparticle measurements identification of the strength as well as type of such interactions is difficult, as some sort of dark-field technique is necessary and it by default only provides scattering data. In plasmonics the typically used criterion to identify strong coupling is a splitting of the single plasmon peak into two with a minimum in the vicinity of the absorption line of the exciton and observation of anticrossing. However, as shown in this work, observation of both effects in scattering does not provide definitive proof and can equally be observed when weak coupling and absorption enhancement occurs. Hence, a correct measurement of such structures requires measurement of absorption in the system.

Papers **6-8** contain measurements, a description, and modelling of coupling in amorphous arrays of nanoresonators and demonstrate how the array geometry influences absorption and scattering of light. Amorphous two-dimensional arrays offer an interesting alternative to periodic structures, as their fabrication only involves bottom-up techniques without resorting to complex lithography techniques. Their topography is determined stochastically by e.g. electrostatic interactions [Fredriksson, 2007], what leads to a minimum separation between nanoparticles and no long-distance correlation. One might think that a lack of periodicity and random placement imply that in an average treatment the properties of amorphous arrays are determined only by the single-resonator properties and that the averaged interaction between them can be neglected. However, as measurements have shown, the optical properties of such arrays exhibit an oscillatory behavior as a function of the minimum center-to-center distance between particles in an amorhpus array. These oscillations are visible in the resonance position as well as the peak width and amplitude (paper **6**). The model, presented in paper **6**, which predicts such behavior is based on a effective polarizability α*

$$\alpha^* = \frac{1}{\alpha^{-1}-S},$$ (5)

where the interaction term $S$ modifies the natural single-particle polarizability. The model is based on the notion that due to averaging of the interactions between particles and a "central one" a picture emerges, in which a central average particle is surrounded by and interacts with a "continuous layer of dipoles (nanoparticles)" with a particular distribution. The interaction term is then of the form

$$S = \pi\sigma \int_{l_{cc}}^{+\infty} e^{ikr}\left(k^2 + \frac{1-ikr}{r^2}\right) G(r,C)dr,$$ (6)

where σ is the surface density of particles of diameter $D$ which depends on the minimum separation between particles $l_{cc}$ and is a function of the corresponding dimensionless parameter $C = l_{cc}D$, $k$ is the

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wave number, $G(r,C)$ is the pair correlation function, and the exponential terms and those in the brackets come from the dipolar Green's function. The function $G$ describes the probability to find another particle at a distance $r$ from a given one and for small $r$ exhibits a particular structure, which assures a minimum separation and at large distances is equal to unity (lack of long-range order). The equation for $S$ for a simplified pair correlation function $G = \Theta(r - l_{cc})$, where $\Theta$ is the Heaviside function but nonetheless preserves the functions most important element – the minimum separation between particles, takes on a simple analytical form

$$S^\Theta = \pi\sigma \frac{e^{ikl_{cc}}}{l_{cc}}(1 + ikl_{cc}).$$  (7)

The term $S$ modifies the single-particle polarizability and as a result changes the resonance position (via the real part of $S$) as well as the peak width and amplitude (via the imaginary part of $S$). Due to the presence of an exponential term both in the real and imaginary parts of $S$ one can identify trigonometric functions with an $l_{cc}$ dependence, i.e. on the minimum center-to-center distance between particles. Performing calculations for the full form of the pair correlation function $G$ one obtains good agreement with experimental measurements and correct predictions of the optical properties of amorphous arrays, namely oscillations of the resonance position (up to 20% of the single-particle value) and the peak width and amplitude (up to 40% of the value).

In paper **7** the above described analytical model is expanded to describe amorphous arrays in both one and three dimensions as well as under arbitrary light incidence and polarization. An important element of this work is also a qualitative description of the optical properties of one-dimensional arrays and an understanding of how their properties are combined when increasing the array dimensionality from one to two and three. Depending on the angle of incidence and polarization, effectively an additional phase shift between subsequently excited resonators, the oscillations of an amorphous array's properties can change amplitude and their period. Additionally, the sole existence of these oscillations can be qualitatively interpreted as "local Fabry-Perot type resonances" in which phase matching hinges on matching the plasmon resonance of an individual nanoparticle with the minimum separation between them, as shown below.

As noted in the introduction, the polarizability of a nanoparticle determines its scattering and absorption cross sections, although in different powers of $\alpha$. Paper **8** is the culmination of the study of amorphous arrays and presents how the interaction within them affects the ratio $R_{s/a}$ of the scattering, $C_{sca} \propto |\alpha|^2$, and absorption, $C_{abs} \propto Im(\alpha)$, cross sections. Substituting these expressions and that for the effective polarizability of amorphous arrays into ratio $R_{s/a}$ one obtains

$$\frac{1}{R_{s/a}} \propto \frac{Im(\alpha)}{|\alpha|^2} + Im(S).$$  (8)

This ratio has a very simple form in which the first term is the single particle ratio and the second term describes the electromagnetic interactions in an amorphous array. Using again the simplified term for $S$ (equation 7) in equation 8 one obtains

$$\frac{1}{R_{s/a}} \propto \frac{Im(\alpha)}{|\alpha|^2} + \frac{\pi\sigma}{l_{cc}}(kl_{cc}\cos kl_{cc} + \sin kl_{cc}).$$  (9)

Equation 9 clearly shows that the modification of the scattering to absorption ratio directly depends on the value of $kl_{cc} \propto l_{cc}/\lambda_0$ (here $k = 2\pi/\lambda_0$, where $\lambda_0$ is the resonance wavelength of a single article), i.e. on the ratio of the minimum center-to-center distance and the plasmon resonance wavelength (the condition for the quasi-Fabry-Perot resonance). The above predictions fully agree with numerical

calculations of amorphous arrays composed of particle of various sizes (i.e. different resonances). Due to the universality of equation 9 the degree of "manipulation" of the scattering-to-absorption ratio is limited and is the same for any nanoparticle. The only "free parameter" here is the range of $R_{s/a}$ ratios one can use. This is determined by choosing the resonance wavelength which directly determines the nanoparticle size (provided all other parameters are fixed).

Based on analytical calculations and numerical modelling presented in paper **8** it is clear, that for small values of $l_{cc}/\lambda_0$ the ratio $R_{s/a}$ is large. A local minimum is observed for $l_{cc}/\lambda_0 \approx 0.75$ and is equal to 0.5 then normalized to the single-particle ratio. These results are thus critical when considering maximizing one of the cross sections. For example, to achieve maximum scattering it is important to use arrays with densities for which the minimum center-to-center distance is not close to 0.75 of the resonance wavelength. To maximize absorption aiming for that value is, however, recommended.

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*5. Description of other research activities*

*Research activities initiated before obtaining the PhD*

The first research topic were metamaterials, i.e. materials whose optical properties are not found in nature. The artificial structure then considered was composed of a unit cell with parallel nanowires which exhibited both electric and magnetic resonances in the near-infrared. These resonances yielded a negative diagonal element in the tensor of the refractive index of the composite material. This work was carried out analytically and numerically, as well at later stages experimentally.

The main research objectives before obtaining the PhD were concerned with nanostructures aperture probes for scanning near-field optical microscopes (SNOM). Such probes have the form of a cut cone

(probe core) whose sides are covered by an opaque metal layer (probe coating) and have sub-100 nm apertures. These probes are used as localized light sources to image optical surfaces with subwavelength resolution. In order to obtain better resolution it becomes necessary to decrease the aperture diameter $d$. Unfortunately, this is accompanied by a decrease in light transmission through the probe which is proportional to $d^{-4}$. In this work a method to increase light transmission through such probes was investigated. The proposed solution uses surface-plasmon polaritons (SPPs) inside the probes, as SPPs have a larger wavevector than free-space light. However, due to the dispersion relation of SPPs launching them inside a "classical" SNOM probe is forbidden. In this work it was proposed to use nano-corrugations of the core-coating interface. Studies have shown that 10-fold transmission enhancement is viable, leading to a ca. 2-fold resolution improvement. Further work, conducted also after being awarded the PhD, yielded a simplified nanostructure design with even greater efficiency. Ultimately, such probes were also fabricated. Directly connected to this topic were studies on SNOM probe radiation in which for the first time a model was proposed which yielded predictions in agreement with experimental measurements. This topic also included apertureless SNOM probes in which the sharp, tapered end of the probe acts as a highly-concentrated localized source of light.

These above-mentioned projects were carried out under the supervision prof. Tomasz Szoplik.

*Research activities initiated after obtaining the PhD*

After receiving the PhD degree work started on a new kind of nanostructured probe with an internal nanostructure tailored to generate magnetic hot spots with subwavelength resolution. The goal behind this endeavor was to design a tool to probe the optical response of optical nanostructures with a magnetic response. The proposed probe consists of a conical dielectric core with azimuthal metallic nanogrooves which support azimuthal plasmons. These azimuthal plasmons after propagating to the aperture generate a strong longitudinal magnetic field at the probe's axis.

The second main topic pursued after being awarded the PhD (in addition to light absorption in plasmonic nanostructures) was and still continues to be plasmonic sensors. The motivation behind this line of research is identification of qualitative and quantitative dependencies of the response of a plasmonic sensor to an external perturbation. The specific goals involve a stochastic analysis of molecule detection at the surface of a sensor and the influence of latter's inhomogeneous field on the quality of detection (counting the number of absorbed molecules, concentration measurements, accuracy in determining binding/unbinding rates, etc.) and modelling detection of structural morphology changes of metallic nanoparticles.

In the last three years were also devoted to the study of nonlocal effects in sub-10 nm nanoparticles made of metals and semiconductors. In parallel work was also carried out on strong plasmon-exciton coupling and on identifying conditions necessary for this strong interaction to occur. This work was conducted in close collaboration with experimental collaborators. Work was also carried out on describing basic optical properties of various types of nanostructures for manipulating the electromagnetic field.