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Plasmonic black metals by broadband light absorption in ultra-sharp convex grooves

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\textbf{Abstract.} We have recently reported broadband (450–850 nm) and efficient (96\% on average) light absorption on gold surfaces with arrays of ultra-sharp convex grooves via excitation and subsequent adiabatic nanofocusing and absorption of gap surface plasmon modes (Søndergaard \textit{et al} 2012 \textit{Nature Commun.} 3 969). Here, we significantly extend our spectroscopy investigations of one- and two-dimensional (1D and 2D) groove arrays in gold covering the wavelength range of 500–1700 nm and report first results on broadband light absorption by 1D groove arrays in nickel. For 1D groove arrays (periods 250 and 350 nm, groove depth 450 nm) in gold, the experimental characterization as well as numerical simulations based on the surface integral equation method reveal gradually increasing reflectivity for wavelengths above \(\sim \) 650 nm reaching finally \(\sim \) 60\% at 1700 nm, but with a remarkable dip around 1150–1250 nm featuring only \(\sim \) 10\% reflectivity. Results indicate that the dip position can be adjusted with the precise groove geometry, a feature that could prove particularly useful for selective thermal emitters in thermophotovoltaics. Furthermore, investigations of field enhancement at the groove bottoms of 1D groove arrays in gold, mapped via

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diffraction-limited two-photon photoluminescence (TPL) scanning microscopy, reveal very selective polarization properties of excitation and TPL emission from the groove bottoms. 1D groove arrays in nickel were fabricated by making parallel 300 nm periodic adiabatic grooves of depths 100, 200, 300, 400 or 500 nm in a 600 nm thick nickel film. Their experimental characterization verifies that the structures are indeed very dark, exhibiting only 5–8% reflectivity over an entire wavelength range 400–1700 nm for the deepest grooves, which is in good correspondence with simulations.

1. Introduction

Metal nanostructures and plasmonics, in general, offer numerous possibilities of new functional materials and advanced configurations, involving radiation guiding, manipulation and nanofocusing beyond the diffraction limit [1], bridging thereby freely propagating photonic modes with surface plasmon polaritons (SPPs) and nm-localized fields [2] and improving also, for example, photovoltaic devices [3]. Composite materials with selective absorption and thermal emission properties have also been suggested, including, for example, ordered arrays of gold-cross resonators placed on a dielectric spacer layer above a planar gold surface [4], ordered arrays of metal elements combining two nanoscale split rings [5], arrays of ultra-thin silver resonant absorbers [6] or random arrays of colloidal metal geometries or nanoantennas [7].

Tapered nanostructures, such as plasmonic V-grooves, involve strong SPP confinement to the groove bottom, for example, used when guiding SPPs along individual grooves [8]. Recently, one-dimensional (1D) gratings of plasmonic V-grooves were treated theoretically [9] and local field intensity enhancement (FE) at the bottom of individual V-grooves has been experimentally characterized and ascribed directly to gap surface plasmon polariton (GSSP) nanofocusing by the closed tapered shape [10]. Although the above experimental characterizations concerned only individual V-grooves at the beginning [8, 10], our first experimental investigations of interacting V-grooves aimed at high FE [11]. We attempted to create a less polarization-sensitive structure by fabricating two-dimensional (2D) periodic arrays of overlapping perpendicular V-grooves and investigated these via scanning two-photon photoluminescence (TPL) microscopy [12] and surface-enhanced Raman scattering (SERS) microscopy [13], thereby directly applying the demonstrated GSSP nanofocusing at the V-groove bottom [11]. In this connection, open periodic V-shaped slits show increased
extraordinary optical transmission [14] due to nanofocusing by the tapering [15] and the FE accessible at the slit bottom has also been characterized [16]. Here it should be noted that the 2D periodic V-groove arrays [11] and 1D periodic narrow slit arrays [16] had periods of 800 and 500–700 nm, respectively, and depths of structures ∼110–180 nm, i.e. still with relatively large flat sections between the grooves causing significant back-reflection.

Recently, in order to collect and guide as much light as possible toward the bottom of closed grooves, we fabricated practically touching ‘V-grooves’ with walls curving toward the groove tip and meeting with a vanishingly small angle [17], ending up with a configuration that is somewhat similar to the so-called kissing nanowires [18]. However, we implemented this groove geometry with the purpose of investigating FE effects when moving from individual V-grooves into a parallel 1D set and, finally, a 2D array of crossing V-grooves, while keeping the parameters of groove depth and the period fixed [17]. During these investigations, we noticed that a part of the structures appeared remarkably dark due to the nanofocusing and relatively large absorption toward the bottom of the deep and thin metallic grooves. In addition, due to the inherent polarization sensitivity of the GSSP excitation in V-grooves (polarization should be perpendicular to the groove), the 1D structures were very polarization sensitive, whereas the fabricated 2D arrays of crossing V-grooves showed high absorption for both in-plane polarizations, appearing dark also for unpolarized illumination [17].

Realizing that the center of the cross configuration was indeed quite dark [17], we started refining the structure to achieve arrays exhibiting the least reflection over a relatively broad wavelength range (mainly in the visible) in order for the structure to really appear black. Consequently, with the desire of getting even higher absorption, we adjusted the depth and period of fabricated arrays until the 1D structures had no flat sections between the parallel grooves and 2D arrays had only sharp dome-like structures left between groove intersections. Both sample geometries made structures appear black for the intended polarizations over an accessible wavelength range 450–850 nm, leading to the very recently demonstrated plasmonic black gold [19], and suggesting also the existence of other plasmonic black metals such as nickel and palladium. The underlying physical mechanism responsible for broadband light absorption in this configuration is related to radiation nanofocusing [20–22], in which GSSPs (excited by scattering of the groove tops) propagate down toward the groove bottoms, being adiabatically squeezed and absorbed in ultra-sharp convex grooves [19].

In this work, we characterize 1D- and 2D plasmonic black gold arrays of high quality, fabricated using focused ion beam (FIB) milling in a 900 nm thick gold film, and we significantly extend our spectroscopy investigations to the relatively wide wavelength range 400–1700 nm assessed experimentally using halogen lamp as well as supercontinuum (SuperK) laser illumination, and theoretically via simulations based on the Green function surface integral equation method for periodic structures [9]. In addition, we employ diffraction-limited TPL scanning microscopy investigations mapping the FE at the groove bottoms of 1D plasmonic black gold and revealing very selective polarization properties of excitation and TPL emission at the narrow groove bottom, similar to those observed in detail with V-grooves [17]. Furthermore, we demonstrate that ‘plasmonic black nickel’ is indeed possible, which is of course already interesting from a fundamental point of view. From an engineering point of view, black nickel is also very appealing since it appears to be easier to achieve (compared to black gold) due to the higher material absorption, which then requires less deep and less sharp grooves to obtain a desired absorption level, and besides nickel has a higher melting point, which would offer increased robustness against thermal damage to the structures.
2. Fabrication of samples

During our initial attempts to fabricate black gold, we decreased the groove period until there were no longer any flat sections between the grooves. At the same time, the intention to mill as deep grooves as possible with FIB led us to the \textit{adiabatic} shape toward infinitely narrow terminations at the groove bottom \cite{19}.

In the first demonstration of plasmonic black gold, we obtained experimental reflection spectra from 1D and 2D black gold arrays \cite{19}. As expected, the 1D arrays exhibited a very large difference in reflection between the p-polarized (electric field perpendicular to the grooves) and s-polarized (electric field parallel the grooves) excitation. On the other hand, the 2D arrays were fabricated with the aim of achieving relatively low reflection anisotropy by milling orthogonally oriented grooves in several passes, while changing the FIB milling direction several times (first two passes along the \(x\)-axis, then two passes along the \(y\)-axis and finally one pass along the \(x\)-axis). The FIB milling was terminated once the top level of 2D arrays started to decrease below the flat gold surface, limiting thereby the groove depths. This procedure was introduced after repeated testing in order to obtain the deepest and most narrow grooves at relatively short periods (compared to the incident wavelengths) and with the best similarity and symmetry between the in-plane \(x\)- and \(y\)-oriented milled grooves, which could be an issue due to slight material re-deposition on the initially milled grooves.

Here we use the above approach to fabricate 1D plasmonic black gold arrays with 250 and 350 nm periodic grooves of depths \(d \sim 450\) nm as well as 2D plasmonic black gold arrays with groove depths limited to only \(d \sim 250\) nm and \(d \sim 400\) nm for the 250 and 350 nm periods, respectively, and all milled in 900 nm thick gold films deposited on fused silica substrates. In addition, we use the FIB to mill 1D ‘plasmonic black nickel’ arrays of parallel 300 nm periodic adiabatic grooves of depths \(d \sim 100, 200, 300, 400\) or \(500\) nm in a 600 nm thick nickel film deposited by e-beam evaporation on silicon substrates.

3. Reflectivity for black gold

Reflection properties of the fabricated arrays were studied using spatially resolved linear reflection spectroscopy \cite{23}. In our very recent work \cite{19}, the plasmonic black gold was demonstrated for the wavelength range 450–850 nm. Here we now exploit a much improved reflection spectroscopy setup that makes it possible for us to investigate the wavelength range 400–1700 nm. The spectroscopic setup included a microscope (BX51, Olympus) equipped with a halogen light source (\(\sim 400–985\) nm) that is now supplemented by a broad spectral range SuperK-laser (SuperK Extreme EXW-4, NKT Photonics) with an 80 MHz fixed repetition rate and driven in constant power mode. The total possible output laser power in visible and near infrared (NIR) wavelength range (500–2400 nm) is \(\sim 2.4\) W, but to avoid thermal damage we adjust the output power to only 6\%. In addition, the collimated and \textit{nearly} unpolarized laser beam with a diameter less than 1 mm is further attenuated using a neutral density filter with 5\% transmission before entering the microscope, thus the total power at the entrance port of the microscope is \(\sim 7\) mW.

Scanning electron microscopy (SEM) images of black gold arrays taken at a tilt angle of 54°, corresponding to normal incidence of the ion beam, reveal only slight variations in the groove period and an ultra-sharp 450 nm deep groove geometry (inset) for the 1D configurations (figure 1(a)), whereas the 2D black gold arrays have sharp dome-like structures left between
Figure 1. SEM images of (a) 1D and (b) 2D black gold 350 nm period arrays, with inset in (a) showing typical 1D groove terminations at the bottom. (c) Optical image of the 2D black gold 350 nm period array (15 × 15 µm²) in microscopes halogen white-light unpolarized illumination (×100 objective). (d) Image of the SuperK-laser spot illuminating a flat gold reference along with (e) its illumination of the 2D black gold array at maintained integration time, both using a ×50 objective. (f) The same as (e) but with increased integration time, ∼30% overexposure.

groove intersections (figure 1(b)). An optical microscope image of the 2D black gold 350 nm periodic array obtained with ×100 objective (numerical aperture, NA = 0.9) and unpolarized halogen light illumination appear very dark though in a slightly greenish color and weak scatterers between groove intersections actually reveal the structure periodicity (figure 1(c)). For better visualization of the SuperK-laser illumination (figures 1(d)–(f)) we decided to use a ×50 objective in order to have a spot size more comparable with the 2D black gold array (15 × 15 µm²). Mapped in true colors, the reflection of the Gaussian distributed SuperK-laser spot at the flat gold film away from structures, almost give associations to a sun (figure 1(d)), whereas illumination of the black gold array really demonstrates the significant broadband absorption intended with these structures (figures 1(e) and (f)). It is important to emphasize that the reflection spectroscopy was performed with the ×100 objective, i.e. with a ∼6 µm spot (evaluated at 600 nm wavelength and level 1/e²) well within the array where no scattering from the edges was observed. The detailed physical explanation for the structured gold surfaces in figure 1 appearing black was given in [24]. Briefly, for the geometry in figure 1(a), the incident light polarized perpendicular to the grooves excites GSSP waves supported by the gaps between groove walls. By an adiabatic groove-tapering design, reflection of GSSPs is avoided such that the GSSPs can reach the bottom ultra-sharp and narrow part of the groove, where it is
subsequently absorbed due to high propagation losses. For the other polarization, no GSSPs exist and reflection will be high, and in fact for longer wavelengths it will not be very different from that of a flat gold surface. Crossed arrays of grooves as in figure 1(b) lead to efficient absorption for both polarizations of incident light by the same mechanism. In this paper, the wavelength range considered will be extended up to 1700 nm. For such long wavelengths, the absorption in gold will be much smaller and thus GSSP propagation losses are less significant.

The image area analyzed by the spectrometer was limited by the diameter of the laser beam, ∼6 µm. The state of polarization was controlled using linear film polarizers (one for visible (400–700 nm) and one for NIR (700–1700 nm)) placed in the beam path just before the microscope objective. Two fiber coupled grating spectrometers were used (in visible: QE65000, Ocean optics and in NIR: AvaSpec-NIR256-1.7, Avantes) in order to measure the linear reflectance in the wavelength range 400–1700 nm. The measured reflectivity spectra were carefully merged around 985 nm (upper limit of visible range spectrometer) to form continuous spectra and all normalized with a ‘perfectly’ reflecting silver mirror (figure 2).

As expected, the reflectivity spectra obtained from the 1D black gold arrays for s-polarized excitation practically resemble that of a flat gold film, whereas p-polarized light is considerably damped for the entire spectrum and with ‘unpolarized’ spectra situated inbetween (figures 2(a) and (b)). The p- and unpolarized spectra of the 1D arrays exhibit a general tendency of increasing reflectivity for longer wavelength, although very significant dips appear in reflectivity at ∼750 and ∼1150 nm for the 250 nm period, which move to ∼850 and ∼1250 nm for the 350 nm period (figures 2(a) and (b)). In fact, increasing the period of 1D arrays from 250 to 350 nm lead to a ∼100 nm red-shift for practically each significant feature in the spectra.

With respect to the 2D black gold arrays, reflectivity spectra obtained using in-plane x- and y-polarized light reveal very successful results for the 350 nm period, whereas the 250 nm period black gold array turned out slightly less impressive for x-polarized light at wavelengths between ∼950–1450 nm (figure 2(c)). The 350 nm period 2D black gold array exhibit very low reflectivity of maximum ∼15% just above 1500 nm, minimum less than ∼1% reflection at ∼700 nm and in average ∼5% for the entire range 500–1700 nm. The 250 nm period 2D array showed an overall average of ∼15% from 500 to 1700 nm, which is still a remarkable result. Both 2D arrays were fabricated with the intention of being fairly symmetric with respect to in-plane x- and y-polarized excitation. This has indeed been successful for the 350 nm period array, while reflectivity from the shorter 250 nm period turned out more asymmetric.
Figure 3. (a) Theoretical reflectivity spectra for ultra-sharp groove arrays with periods $\Lambda = 250$ or 350 nm, depth 450 nm and groove profiles shown as insets. (b) Theoretical reflectivity spectra for two groove arrays with period 250 nm for either a groove geometry of depth 450 nm (dashed curve) or of depth 460 nm (dash-dot curve), where the latter is the same groove except that a groove section of 10 nm length and 1 nm width has been added to the groove, and reflectivity spectrum for the geometry corresponding to repeatedly interchanging each type of groove (solid curve). (c), (d) Theoretical reflectivity spectra for ultra-sharp groove arrays with periods $\Lambda = 250$ nm, depth 450 nm and groove profiles shown as insets.

However, one should keep in mind that for 2D arrays, the FIB milling direction was changed several times between the passes, for which the shortest 250 nm period will be more sensitive to possible minor misalignments and re-deposition of milled-away material into neighboring grooves, thereby compromising the adiabatic shape.

In general, the physics of plasmonic black metal is quite clearly discussed [19, 24], while deviations appear due to none of the fabricated grooves being completely identical. To support the experimental 1D characterization, we have also calculated reflectivity spectra for a wide range of groove geometries with a Green function surface integral equation method similar to our recent work [19, 24] but for a much wider wavelength range. In the calculations, light is p-polarized and normally incident on a periodic array of grooves in a gold surface with the refractive index of gold taken from [25]. Two selected examples of reflectivity spectra are shown in figure 3(a) for periodic arrays of ultra-sharp grooves of depth 450 nm and periods $\Lambda = 250$.
and 350 nm, respectively. Near the groove bottom the groove width is tapered down until it reaches a width of 0.3 nm, i.e. the size of a gold atom, and there the shape of the groove bottom is rounded off with a half-circle. The actual groove profiles are shown as an inset. Note that the very fine details of the groove shape, especially near the groove bottom, which will also influence significantly the reflectivity spectra, are not visible on this scale. Notice the reflectivity dip at wavelengths near 1150 nm ($\lambda = 250$ nm) or 1250 nm ($\lambda = 350$ nm) similar to the experimental results in figures 2(a) and (b), and another reflectivity dip at wavelengths near 800 nm, which is also similar to the experiments. These reflectivity dips are not as deep as those measured but at least they are at approximately the same wavelengths. Actually, having these reflectivity dips positioned at those particular wavelengths in the theoretical calculation was achieved only after trying out a large number of groove designs and step-by-step adjusting the actual groove shape to move reflectivity dips to those wavelengths. As a general rule, keeping the groove depth fixed, the reflectivity dips can be moved to longer or shorter wavelengths by making the grooves more or less narrow (figures 3(c) and (d)). The examples in figure 3(d) illustrate that, compared with figure 3(a), we found in many cases that if we make grooves more narrow, and thereby move reflectivity dips to longer wavelengths, the reflectivity dips can also become significantly deeper than those seen in figure 3(a), but there will be too many reflectivity dips to get a match with the two dips seen in the experiments, and we were unsuccessful in achieving deeper reflectivity dips matching both the depth and wavelengths of those measured experimentally. The measured reflectivity dips are also spectrally wider than those calculated in figure 3(a).

We will argue here that a plausible explanation for the measured reflectivity profiles in figure 2 must include the effect of variations in the surface geometry beyond those of a perfectly periodic groove array. It is clear that, one should not expect for the fabricated grooves to be identical with nm accuracy, which is beyond the current fabrication technology, while on the other hand, tiny variations especially at the groove bottom are of critical importance for the reflectivity. To support this, we give an example of calculated reflectivities in figure 3(b) where the dashed curve is the same as in figure 3(a) for the geometry with period $\Lambda = 250$ nm, and the dash-dotted curve corresponds to the reflectivity from a geometry where the groove depth has been increased by 10 nm by inserting an additional straight groove section of width 1 nm. Inserting this groove section results in a slight but noticeable shift in the reflectivity dips. The groove geometries are shown as insets and on the scale shown here the difference is barely noticeable. We have also shown a calculation (solid curve) where we consider a geometry consisting of interchanging each type of groove repeatedly such that the resulting unit cell period is 500 nm and contains two grooves where one is of the dashed and the other of the dash-dotted type. Notice that this geometry has a very deep reflectivity dip at wavelengths near 800 nm such that this part of the reflectivity spectrum is very similar to that measured in figure 2(a). Clearly, we do not just get the average of the dashed and the dash-dotted curves. This can be understood by considering that the reflection phase for each type of groove can be different such that even if the reflectivities are similar for the two types of grooves considered separately, the reflectivity for the combined geometry consists of a contribution from each type of groove that can be out of phase and thus cancel each other.

For applications, the adjustable high absorption windows at NIR wavelengths might be used in reverse for controlled thermal emission [26] right where most photodiodes are sensitive, whereas the shape of black body emission render the first dips below 850 and 750 nm less significant.

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4. Two-photon photoluminescence microscopy of black gold

Although FEIs from nm-gaps of individual [10] and crossing V-groove structures with similar geometries were investigated [17], so far no direct characterization of FEIs exhibited within the adiabatic grooves of large-area plasmonic black gold configurations was performed, while it could actually reveal SERS possibilities in line with observations for 2D periodic V-groove arrays [11]. One well-established experimental technique for the evaluation of FE in nanostructures is TPL from metals, which was earlier described [27, 28], with spatially resolved TPL studies [29, 30] and near-field imaging [31] used for characterization of local FEIs.

We have previously used TPL scanning optical microscopy to facilitate direct estimations of the local FE (at a diffraction-limited resolution) achieved with various types of samples, for example, individual metal nanostraps [32]. Our experimental setup for TPL microscopy is essentially the same as that described in detail for previous experiments [33]. It consists of a scanning optical microscope in reflection geometry built on the base of a commercial microscope and a computer-controlled 2D piezoelectric translation stage. The linearly polarized light from a mode-locked pulsed (pulse duration \(\sim\) 200 fs, repetition rate \(\sim\) 80 MHz) Ti-sapphire laser (\(\lambda = 730–850\) nm, \(\delta\lambda \sim 10\) nm) is used as a source of sample illumination at the fundamental harmonic (FH) frequency. The illumination power was selected in the range 0.4–2 mW, depending on wavelength, polarization and the obtained TPL signals. The TPL radiation generated in reflection and the reflected FH beam are collected with the same objective, separated by a wavelength selective beam splitter, directed through appropriate filters and detected with two photomultiplier tubes, the tube for TPL photons being connected with a photon counter obtaining usually less than 10 counts per second (cps).

Typical polarized FH and TPL images, recorded partly inside the 1D 350 nm period black gold array and partly outside the array at the flat gold film, facilitates direct comparison of the structured and unstructured surface (figures 4(b)–(e)), while an SEM image (figure 4(a)) indicates the array orientation and relative position. The selected parallel polarization configuration of incident FH and detected (FH or TPL) light is indicated by the set of arrows on the corresponding images (figures 4(b)–(e)). Due to the relatively short period, we are unable to resolve individual grooves in neither the FH or TPL images (similarly for 250 nm period, not shown).

Here, the FH images appear bright at the reflecting smooth gold and darker at the black gold, whereas the TPL images exhibit the opposite behavior. At the same time, the images also indicate the well-defined polarization dependence, clearly distinguishing the excitation of GSSPs in the grooves at p-polarized illumination (figures 4(b) and (c)) from that of non-exciting s-polarized groove illumination (figures 4(d) and (e)). For p-polarized illumination, the black part of the FH image is directly related to a strong absorption in the adiabatic grooves, whereas the slight darkness observed for s-polarized illumination should be related mainly to increased scattering by imperfections at the structured surface. Conversely, the TPL images appear brighter at grooves, especially for the p-polarized configuration supporting the excitation of GSSPs into the grooves and detection of TPL signal emitted from the groove bottom via GSSPs supported again for the same polarization, as recently verified directly for the related groove geometries [17]. For an incident power of less than 0.4 mW, the obtained TPL signal for resonant p-polarized excitation was \(\sim\) 350 cps, which is comparable to that obtained with V-groove geometries [11]. At the same time, for s-polarized configurations, the much weaker TPL signals obtained from the structure should also be expected based on the absence of dips.
Figure 4. (a) SEM image from a 1D black gold array having period 350 nm and groove depth 450 nm along with (b), (d) FH and (c), (e) TPL images obtained at excitation wavelength $\lambda \sim 740$ nm. The imaged area is $9.7 \times 3 \, \mu\text{m}^2$ and the polarization configuration of excitation (FH) and detection (FH or TPL) is indicated by double arrows in (b)–(e). (f) Averaged cross-sections along the FH and TPL images in (b)–(e), as well as from the corresponding images (not shown) for the 250 nm period array, and with legend extensions p and s referring to the polarization configuration.

in the corresponding reflection spectra (figures 2(a) and (b)), resembling those of a smooth gold region away from field enhancing structures and leading in general to the relatively weak TPL signals. In this connection, one should note the dark spot at the upper right corner of the FH image (figure 4(d)) and corresponding brighter TPL spot observed for s-polarization (figure 4(e)), which can be ascribed to an array defect or impurity, although not nearly bright enough to immediately show up in the perpendicular p-polarized configuration. On the other hand, in accordance with recent investigations [17], the TPL signal originating from the nm-gaps at the groove bottoms turn out to be p-polarized due to the emission via GSSPs, i.e. the main TPL signals from black gold are extinguished for the crossed (p-polarized excitation, s-polarized detection) configuration, while TPL signals originating from surface defects were maintained also for cross-polarized detection.

The simultaneous recording of TPL and FH signals as a function of scan coordinates results in correlated FH and TPL images (e.g. figures 4(b) and (c)) and facilitates direct comparison of FH and TPL cross-sections (figure 4(f)). As expected, the cross-sections of FH images obtained in the parallel-polarized configuration of excitation and detection at wavelength $\lambda \sim 740$ nm clearly demonstrates the decreased reflection down to $\sim 8\%$ from the black gold array for p-polarized light, and only a barely visible influence for s-polarized light, i.e. in good agreement with reflection spectra obtained using the SuperK-laser (figure 2(a)). At the same time, the TPL signal is practically visible only for p-polarized light and only from the black gold area.
Applications of TPL scanning optical microscopy for characterization of local FE (of the incident FH radiation) in gold nanostructures can be considered well-established [23, 34, 35]. Quantitative evaluation of FEs can be carried out by comparing TPL signals from the groove array to that from a smooth gold film [12, 34]. Following this approach, the FE factor \( \alpha \) can be written as

\[
\alpha^2 = \frac{\text{TPL}_{\text{grooves}}(P_{\text{ref}})^2 A_{\text{ref}}}{\text{TPL}_{\text{ref}}(P_{\text{grooves}})^2 A_{\text{grooves}}},
\]

where TPL is the obtained TPL signal, \( \langle P \rangle \) is the used average incident power and \( A \) is the area producing the enhancement. Meanwhile, when considering more complex structures with the spatial variations extending also in depth, for example, narrowing like V-grooves, one should also take into account the limited accessibility of both FH excitation and (polarized) TPL emission, as recently demonstrated directly with V-grooves [17].

With this in mind, we proceed with a rough estimate of the FE based on typical TPL levels emitted from the narrow gap of the grooves using \( A_{\text{ref}} \) as the area of focused FH beam cross-section, i.e. \( A_{\text{ref}} \approx \pi (0.35 \mu m)^2 \), whereas \( A_{\text{grooves}} \) is estimated as a part of the grooves closest to the bottom, where the expected FE is largest [19] and being illuminated within the focused FH spot. Supported by simulations of the field magnitude distributions in black gold grooves [19], we estimate the effective width actually producing TPL as two times the projection of the lowest 1/3 of groove side walls corresponding to \( \sim 25 \) nm, resulting in an area \( A_{\text{groove}} \approx 0.025 \mu m \times 0.7 \mu m = 0.0175 \mu m^2 \), i.e. an area reduction of \( \sim 22 \) compared to that of the reference. Via calibrated TPL signals obtained from smooth gold film regions (e.g. \( \sim 1.1 \) kcps at \( \lambda \sim 740 \) nm and incident FH power of \( P_{\text{ref}} = 15 \) mW), we obtain typical FE factors of up to \( \sim 112 \) for the p-polarized excitation of the 250 nm period array. Applying the similar approach for the 350 nm period array, we obtain \( \sim 100 \), which is actually in qualitative agreement with the increased reflectivity around 740 nm for this structure (cf figures 2(a) and (b)).

5. Reflectivity for black nickel one-dimensional arrays

To experimentally demonstrate the blackening by plasmonic nanofocusing in adiabatic grooves [19], also for other metals than gold, we used the FIB to fabricate 1D 300 nm periodic arrays (20 \( \times \) 20 \( \mu m^2 \)) of parallel grooves in a 600 nm thick nickel film. At first we demonstrate black nickel arrays fabricated with fixed depths of either 200 or 500 nm using FIB milling currents of 20 and 100 pA, respectively. SEM images of the 1D black nickel structure revealed groove arrays nearly without defects and with only minor deviations from the period (figures 5(a) and (b)). The quality of the flat nickel film away from structures also appeared practically without undesired particles, although with slightly more surface roughness than the gold films. Optical microscope images of the 1D arrays, obtained for p-polarized illumination using \( \times 100 \) objective, demonstrate that black nickel structures with 500 nm deep grooves certainly appear black and even the only 200 nm deep grooves show considerable effect on reflection (insets of figures 5(a) and (b)). The few slightly brighter and parallel lines in the optical images correspond to minor irregularities from the FIB written period causing relatively larger flat nickel sections between some grooves.

Since these are the first results with the ‘plasmonic black nickel’ configuration, we started our optical reflection spectroscopy [23] using the halogen light source in order to get reflection...
spectra (figure 5(c)) of the fabricated 1D black nickel arrays directly comparable to those obtained from black gold [19]. Note, however, that we have now extended the available wavelength range to 400–985 nm by using separate polarizers suitable for the visible and NIR parts of the spectra, respectively. Furthermore, wavelengths in the range 400–500 nm cannot be reached with the SuperK-laser. The image area analyzed by the spectrometer was limited by an iris with a diameter down to 1 mm resulting in a circular probing area with a diameter of 10 µm.

The reflectivity spectra obtained from the black nickel structure certainly appear very promising with down to only \( \sim 5\% \) reflectivity for the deepest 500 nm grooves at p-polarized excitation (figure 5(c)). For s-polarization the reflection from 500 nm grooves is still less than that from flat nickel, most likely due to increased scattering from the imperfections along the grooves. On the other hand, the 200 nm deep groove array is exhibiting practically the same reflectivity as flat nickel for s-polarization, but still already quite remarkable low reflectivity of only \( \sim 20\% \) for p-polarization (figure 5(c)).

To increase the experimentally investigated wavelength range also for black nickel, we then used the SuperK-laser for reflection spectroscopy (figure 6(a)) and compare with theoretical Green’s function surface integral equation calculations for periodic arrays of ultra-sharp grooves in nickel, with the corresponding 300 nm period and the range of groove depths from \( d = 100 \) to 500 nm (figure 6(b)). In the calculations light is normally incident, p-polarized with respect to the grooves, and the refractive index of nickel is taken from [36]. First of all, one should notice the extremely low \( \sim 5\% \) reflectivity obtained for the deeper 400 and 500 nm black nickel arrays, and overall good qualitative agreement with the simulations. For the visible wavelengths the predicted simulated reflectivity tend to be a bit lower, whereas for the NIR range the experimentally obtained reflectivity is actually even lower, for example, this is particularly apparent for the 300 nm deep array. One explanation for this effect could be the wavelength-dependent ratio between scattering and absorption efficiencies for certain (fixed) nm-sized imperfections/roughness not present in the simulations, i.e. for shorter wavelengths scattering (at the surface and out of the structure) from such imperfections could dominate over their absorption leading to experimentally less efficient focusing into the adiabatic black nickel.
structures, while for longer wavelengths absorption from these imperfections could dominate and even increase the efficient absorption toward the structure bottom.

In the theoretical reflectivity spectra (figure 6(b)), for example, for the groove depth of $d = 200$ nm, there is a minimum in the reflectivity at the wavelength 600 nm. This minimum is also observed in the experimental result in figure 5(c), but not in the experimental result in figure 6(a). This slight difference in the experimental results we explain as a result of the measurements being made on two slightly different positions on the black nickel sample. In the theoretical result (figure 6(b)), there is a flat plateau at the groove top of width 100 nm when the depth is $d = 500$ nm (see surface geometries in the inset), and it is 145 nm when the depth is $d = 200$ nm. The decreasing plateau width with increasing groove depth reflects that when the fabricated grooves are deeper they also become wider near the top of the grooves. If we remove the flat plateau and use a wider groove near the groove top instead then, for example, for the groove depth of 200 nm, we no longer have a minimum reflectivity at the wavelength 600 nm. For short wavelengths, practically, all light coupled into the grooves is absorbed and the light is mainly reflected due to the presence of the plateau. In that case, larger plateaux lead to larger reflection. For longer wavelengths, where nickel is a less efficient absorber, the absorption in the grooves will increase with the increasing plateau width since that also leads to grooves that are more narrow with resulting increased propagation losses of GSSPs. Thus, for longer wavelengths, a plateau can be favorable for suppressing reflection. Furthermore, in that case the reflectivity will generally be reduced (further) below the measured reflectivity in figures 5(c) and 6(a) while the reflectivity will be increased for the longer of the considered wavelengths at the same time. In this case of nickel instead of gold, we obtain rather good agreement between theory and experiments without mixing grooves of slightly different shapes in the theoretical calculation. The smaller sensitivity to the precise geometry is a consequence of the higher absorption losses in nickel compared with gold.
It is apparent that the black nickel structures offer an excellent and relatively cheap (compared to gold) plasmonic broadband absorber. Furthermore, given the demonstrated relatively large difference in reflectivity for p- and s-polarized light incident on the 1D black nickel arrays (figure 5(c)), it is also likely that these structures could serve as broadband polarizers, operating in reflection and at efficiencies possibly improved via arrangements of multiple structures. At telecom wavelengths, the reflectivity for s-polarized light is 70–80% and still only ∼5% for p-polarized light, leading to extinction ratios of around 14–16 for each reflection. In addition, the higher melting point of nickel (∼1453 °C) compared to gold (∼1063 °C) could facilitate increased operational temperature range of the black nickel devices.

6. Discussion: SuperK versus halogen illumination

Regarding the applied reflection spectroscopy setup, the illumination configuration and measurement conditions are fundamentally different depending on the use of either the SuperK-laser or the halogen lamp. Applying the halogen lamp, we illuminate a large area under all angles up to 64°, and detect all angles up to 64°, within a circular area (diameter 10 µm) selected in detection by the iris, i.e. with the halogen lamp we achieve a homogeneous illumination of an investigated larger sample area, hence averaging over this larger area. On the other hand, using the SuperK-laser, we illuminate angles up to ∼10° (approaching normally incident) and detect all angles up to 64° (NA = 0.9), within an area limited by the illumination spot ∼6 µm (not iris). In this connection, it should be noted that, for the case of plasmonic black gold, supplementary information of [19] actually revealed only minor influence of excitation angles up to at least 40° (NA = 0.65). However, the SuperK-laser also lead to a Gaussian intensity distribution in the illumination spot, i.e. a more inhomogeneous illumination and less averaging from a smaller spot size, but then at the same time spatially coherent. This spatial coherence could be particularly important for the longer wavelengths, where reflection from the plasmonic black metal structures are in general higher and with phase relations possibly leading to additional interference peaks or dips. All in all, these issues might also explain the minor differences in results obtained, e.g. for black nickel when using either the SuperK or halogen illumination (cf figure 5(c) versus figure 6(a)).

7. Conclusion

In conclusion, we have performed spectroscopic investigations of 1D- and 2D plasmonic black gold, for the wavelength range 500–1700 nm using SuperK-laser illumination. For 1D black gold arrays, the experimental characterizations as well as simulations based on the surface integral equation method revealed gradually increasing reflectivity for wavelengths above ∼650 nm reaching finally ∼60% at 1700 nm, but with a remarkable dip around 1150–1250 nm featuring only ∼10% reflectivity. Results indicate that this dip position of high absorption can be adjusted with the precise geometry as well as curvature at the top part of the grooves, i.e. a feature that could prove particularly useful for selective thermal emitters within thermophotovoltaics. Furthermore, investigations of FE at the groove bottoms of 1D plasmonic black gold, mapped via diffraction-limited TPL scanning microscopy, revealed very selective polarization properties of excitation and TPL emission at the narrow groove bottom. Additionally, we have fabricated 1D ‘plasmonic black nickel’ of parallel 300 nm periodic adiabatic grooves of depths 100, 200, 300, 400 or 500 nm in a 600 nm thick nickel film.

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and experimentally verified that the structures are indeed very dark, exhibiting only 5–8% reflectivity over the entire range 400–1700 nm for the deepest grooves and being in good correspondence with our simulations. Hence, black nickel could function as an excellent and relatively cheap (compared to gold) plasmonic broadband absorber, and in particular the 1D configurations could also serve as broadband polarizers operating in reflection.

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