Plasmon-Induced Disorder Engineering for Robust Optical Sensors

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Optical metasurfaces address a plethora of applications in planar optics, as they enable precise control of the phase, amplitude, and polarization of light at nanoscale interaction lengths. However, their implementation requires surface nanostructuring, based on complex design and fabrication methods. In addition, exploiting narrow spectral features, e.g., for sensing, is accompanied by high demands in terms of precise post-process alignments of probing light—impractical for compact optical systems. Here, the realization of plasmonic metasurfaces, based on silver nanoparticles (AgNPs) and using a solution-based growth method, is demonstrated. The particle growth is mediated by localized surface plasmon resonances. The resulting nanostructures are directly applicable as self-optimized metasurfaces in optical systems, as their fabrication and probing procedures allow the use of common—photonic and plasmonic—platforms. Information regarding the electromagnetic (EM) environment is stored during the fabrication via distinct particle positions and dimensions. The resulting optical response is inherently sensitive to deviations from this EM environment—enabling high-performance nanoplasmonic sensing with a maximum discrete Figure of Merit* (\(\text{FoM}^\text{max}\)) of 968 without the need for post-process alignments.

1. Introduction

Metal nanoparticles (NPs) support localized surface plasmon (LSP) resonances that enable immense electromagnetic field enhancement inside nanoscale volumes.[3] Astonishing optical properties arise in the case of noble metals, as the LSP resonance is spectrally located within the visible to near-infrared regime. Not only are the resonance conditions inherently sensitive to the dielectric environment, but they can also be manipulated via the particle’s size and shape.[4] As a result, plasmonic metal NPs have gained remarkable attention in numerous research fields of optics, including surface-enhanced Raman spectroscopy,[5–6] solar energy harvesting,[7–8] nonlinear optics,[6] and nanoplasmonic sensing.[9–10]

In the latter case, an isolated metal NP does not implicitly define an excellent sensor. High intrinsic absorption losses of metals and radiation damping due to scattering impair their performance. In consequence, the corresponding quality factors Q are limited (typically Q in the order of 10), which is well below what is required for many sensory applications.[9] The 2D assembly of metal NPs, forming plasmonic metasurfaces of subwavelength thickness, counteracts this drawback since a collective response of multiple particles may reduce radiative loss.[10] Common assembly designs contain a certain degree of deterministic order (e.g., periodicity). In this context, numerous reports demonstrate sharp spectral features, such as Fano resonances,[11–12] or, more recently, surface lattice resonances,[13–15] featuring high-quality factors. However, the resulting high sensitivity toward refractive index (RI) changes also implies a low tolerance for deviations with respect to the incident angles (azimuthal and polar angle) of probing light. Furthermore, implementing nanostructures of excellent quality requires complex design routines and fabrication procedures, such as electron beam lithography (EBL) or focused ion beam (FIB) techniques. Thus, exploiting high-Q resonances supported by ordered nanostructures within integrated optical systems remains challenging, due to cost- and labor-intensive top-down fabrication, as well as extensive requirements for post-process alignments.

While sharp spectral features, e.g., resonances, are commonly linked to ordered structures, nowadays a different type of spatial system challenges this assumption—a system that promises either to compete with the performance of ordered systems or, even, to circumvent issues that are related to order, such as diffraction artifacts.[16] This class of nanostructures lies between perfect order and complete randomness—structures of engineered disorder.[10] Besides their performance, disorder intuitively suggests a more facile way of fabrication. However, structures of engineered disorder also demand high position accuracies of structural elements, in order to achieve...
the desired optical response. In fact, the perfect engineered disorder can be even more difficult to realize, due to the high complexity of the corresponding design routines.

Self-organization of nanostructures has, in turn, proven itself as a promising bottom-up approach for more facile manufacturing procedures. In the past, this has been used for many purposes in ordered and disordered systems, with applications including solar cells,[27] organic lasers,[18] broadband plasmonic absorbers,[19] plasmonic crystals,[20] and flexible electronics.[24]

Among various strategies that enable self-organization of nanostructures,[22–24] the light-controlled growth of AgNPs at distinct positions on a transparent substrate via the excitation of LSP resonances is one promising approach. Under large-angle incidence of s-polarized light, the absence of a significant lateral field strength largely suppresses coupling between LSP resonances. Nevertheless, we have shown, that even in this case such isolated silver nanoparticles can generate a nanostructure of engineered disorder,[25] which is governed by the light source.

In this paper, we examine the opposite scenario. Surface plasmon polaritons (SPPs) with their longitudinal electric field are excited to ensure a maximum coupling of LSP resonances. In consequence, a long-range structuring is introduced, which—reciprocally—enables k-space engineering with much sharper features.

The resulting plasmonic metasurfaces, grown from solution, are directly applicable as optical RI sensors and are both instantaneously tailored and intrinsically aligned to the probing light source. Given the fact that the fabrication procedure is based on an attenuated total reflectance configuration, the application of the metasurfaces as nanoplasmonic RI sensors changes the paradigm of distinct fabrication and probing scenarios. The resulting performance of the sensor (FoMmax = 968) is found to be superior compared to numerous state-of-the-art plasmonic sensors based on complex and cost-intensive nanofabrication procedures.[19] The quality of the structure, and thus the sensing performance, is concluded to depend only on the lasers’ divergence. Thus, to obtain an optical sensor of higher performance, only a more parallel laser beam is required. Because of its versatility and high performance, along with cost-efficiency, this approach is foreseen as initiating a shift of focus from top-down (e.g., EBL) towards cost-efficient, bottom-up fabrication methods in the field of functional plasmonic metasurfaces.

2. Results and Discussion

First, we discuss the principle of the plasmon-induced growth and the optical probing of our disorder engineered metasurfaces. In Figure 1a, the instantaneous surface nanostructuring based on the electroless deposition (ELD) technique is visualized. A detailed description of the sample fabrication can be found in the Experimental Section. Initially, SPPs scatter from surface imperfections or from randomly grown seed particles. The scattered waves interfere and generate positions of maximized local electromagnetic field intensity. At such positions (emphasized as red ellipses on the sample’s surface), the growth rate of AgNPs is enhanced. After a nanoparticle has reached an over-critical size, it serves as an additional, efficient scatterer of electromagnetic waves (photons and SPPs) and additional intensity hotspots are generated. This visualizes the capability of instantaneous nanostructuring (emphasized by white lines between the particles indicating the formation of a network) to adapt to an EM environment with a certain RI (λSPP = λSPP (nana-
lyte)) and the specific wavefronts of a well-aligned light source. A detailed description of λSPP(nanalyte) is shown in the Supporting Information.

After the deposition procedure, the ELD solution is removed from the sample’s surface. An additional flow cell, attached to the sample, now enables the continuous exchange of a test analyte (Figure 1b). The change of the analyte’s RI inside the flow cell is constantly monitored using a Michelson interferometer (see Supporting Information) during the entire measurement.

The resulting reflectance of the sample is shown in Figure 1c. Starting at a RI of water (nH2O = 1.333), the reflectance first follows a SPP resonance curve. At the position, which corresponds to the EM environment during the particle growth (n = nELD), a narrow peak in reflectance is observed. The reflectance increases from approximately 44% to 52%. According to the data obtained from the Michelson interferometer, the full width at half maximum (FWHM) of this peak is measured to be ∆n0 = 3 · 10−4, which is about two orders of magnitude narrower, than the theoretical FWHM of the SPP resonance.

To investigate the origin of this optical response, we first discuss the spatial dimensions and arrangement of the particles. Figures 2a,b show scanning electron micrographs of the grown nanostructure and structural elements. From the real-space image, the spatial distribution of the particles appears to be random. However, the Fourier-transformed electron micrograph (FTEM) reveals an engineered disorder of AgNPs. Two
pronounced (dark) rings (hereinafter referred to as structure rings) that touch each other at \( x^{-1}, y^{-1} = 0 \) are observed in the FTEM (Figure 2c). From photonic excitation similar but much less pronounced features are known. In those studies, it has been found that the mirror-symmetric shift \( r_{\text{in}} \) along the \( x^{-1} \)-axis refers to the incident wave while the radii of these rings \( r \) refer to the scattered waves.\(^{[25]}\) In contrast to photonic excitation, under SPP excitation in all experiments the circles have always been found to touch each other with

\[
r_{\text{in}} = r = 1/\lambda_{\text{SPP}}
\]

That means that SPPs dominate the self-organization of AgNPs including the excitation \( (r_{\text{in}}) \) and the circular scattering \( (r) \) in the \( x-y \)-plane. Remarkably, photonic features are not found in the FTEMs. Further, it is observed, that the average particle radius is 92 nm (see Figure 2d). Figure 2e shows an optical image of the sample after the deposition of AgNPs.

Next, we focus on how the k-space of the structure is linked to its optical response. After the growth, information regarding the incident SPP wave (shift) and the scattered SPPs (radii) are permanently stored within the metasurface. The resulting structure rings in the FTEM indicate a reduced scattering probability under excitation with the exact SPP wavelength, which was used for the growth. In our configuration, this reduced forward scattering into the free space, in turn, yields an increased back reflection under growth conditions. When the RI, and thus the SPP wavelength, is changed, the dark structure rings remain constant. However, this change of the environment can then be described by rings in the k-space whose radii scale linearly with the effective RI, termed as wave rings (see Equation 1). As these wave rings represent both the initial state before scattering as well as the goal states the measured reflection can simply be modeled by an overlap of the structure and the wave rings. These new wave rings do not perfectly overlap with the structure rings, so with the states of reduced scattering probability, anymore. In consequence, scattering is increased when the RI is changed in comparison to the growth conditions.

To simulate this overlap function, the width of both the structure and the wave rings must be evaluated. Afterwards, the radii of the wave rings are continuously increased depending on the RI and their overlap with the structure rings is calculated. The width of the wave rings is governed by the laser divergence (see Supporting Information). The measured laser divergence yields a momentum width of the wave rings of \( \Delta r_{W} \approx 1.72 \times 10^{-4} \) \( \mu \text{m}^{-1} \) (FWHM). The momentum widths of the structure rings \( \Delta r_{S} \) for observation windows between 92 \( \times \) 92 \( \mu \text{m}^2 \) and 148 \( \times \) 148 \( \mu \text{m}^2 \) size are measured from the FTEMs. However, the metasurfaces are homogenous over the entire illuminated area of about 33.4 \( \mu \text{m}^2 \). Due to the uncertainty principle, the width of a feature in the FTEM is reciprocally linked to the size of the observation window in the real space. Thus, to compare the results from the optical measurements, where the entire deposition area is illuminated by the laser, with those of the FTEMs, a corrected momentum width of the structure rings \( \Delta r_{S,C} \) has been calculated as \( \Delta r_{S,C} \approx 5.97 \times 10^{-6} \) \( \mu \text{m}^{-1} \) (see Supporting Information for more details).

In Figure 3a, the principle of overlapping the structure rings with \( \Delta r_{S,C} \) and the wave rings with \( \Delta r_{W} \) is emphasized. Starting with wave rings that correspond to an RI of water \( (n_w) \) used as initial analyte (small red rings of radius \( r(n_w) \)), the wave rings expand with an increasing RI up to a final value \( n_f = 1.34 \) (large red rings of radius \( r(n_f) \)). Both rings are modeled with a Gaussian intensity profile (see Supporting Information). The widths (FWHM) of the two modeled rings are given by the measured values for \( \Delta r_{S,C} \) and \( \Delta r_{W} \). Then, we calculate the overlap of the two rings as a function of the refractive index.

Figure 3b shows the measured reflectance with a distinct feature at the RI representing the growth conditions of the structure. A fit to this characteristic assuming a pure SPP resonance with the structure treated as effective homogeneous layer (see Supporting Information) is shown in Figure 3c (black curve) together with the overlap function (red curve). The width of the arising peak at the growth conditions is found to be \( \Delta n_g \approx 2.9 \times 10^{-4} \) (FWHM). In combination, these two characteristics (SPP resonance fit and overlap function) are concluded to yield the overall optical response of the metasurface.

In the next step, we investigated the sensing performance of the metasurface by calculating the discrete Figure of Merit*
Figure 3. Origin of the sensitivity towards changes in the dielectric environment of the metasurface: a) Principle of overlapping the fixed structure rings with the wave rings as a function of the RI; b) Measurement of the reflectance of the sample dependent on the RI in close proximity to the growth conditions; c) Resulting overlap function (red) with a distinct peak at the RI corresponding to the growth conditions and the underlying fitted SPP resonance (black curve).

(FoM*), on the basis of the measured data. The FoM* is given by

\[ \text{FoM}^* = \frac{1}{I} \left[ \frac{\partial I}{\partial n_{\text{analyte}}} \right] \]  \hspace{1cm} (2)

where \( I \) is some measured intensity signal (here the reflected laser beam) at a fixed wavelength \( \lambda_0 \), \( n_{\text{analyte}} \) is the refractive index of the analyte surrounding the grown metasurface, and \( \frac{\partial I}{\partial n_{\text{analyte}}} \) is the change of the measured intensity with respect to a change in \( n_{\text{analyte}} \).[26]

With a FoM\(_{\text{max}}\) of 968, the self-optimized nanoplasmonic sensor is found to have a superior performance compared to numerous plasmonic systems fabricated by cost- and labor-intensive, top-down fabrication methods.[27–30]

We have seen that the width of the overlap function and thus the structural feature in the optical response depends on the widths of the structure rings and the wave rings. In turn, these are both governed by the laser’s divergence. Therefore, it is further concluded that the performance of the sensor only depends on the laser’s divergence—and thus, for a constant deposition area, a more parallel laser beam yields a sensor of higher performance.

Finally, we discuss the impact of mechanical misalignments of probing light. During these experiments, it has been observed that even slight mechanical misalignments after the deposition procedure result in the loss of the structure’s functionality. To investigate actual tolerance for mechanical misalignments, we simulated the overlap function of the structure rings and the wave rings while changing the incident angle of probing light both in azimuthal and polar direction.

Figure 4. Tolerance for mechanical misalignments and sensitivity towards changes in the probing wavelength: a) principle of deriving the overlap function with respect to mechanical misalignments in azimuthal angle and polar angle; b,c) effect on the overlap function of the structure and the wave rings towards changes in the azimuthal angle \( \Delta \phi \) and changes in the polar angle \( \Delta \theta \); d) overlap function with respect to the incident wavelength \( \lambda \).
In Figure 4, the tolerance of the maximum overlap of structure and wave rings is shown with respect to misalignments of both angles respectively.

The simulation results show that the overlap of the structure and wave rings possesses a low tolerance for mechanical misalignments in the azimuthal and polar angle. The maximum overlap decreases by approximately 50% for a misalignment of $\Delta \varphi = 0.012^\circ$ and $\Delta \theta = 0.024^\circ$ in the azimuthal and polar angles respectively. However, to obtain a high sensitivity towards RI changes, a significant overlap of the structure rings and the wave rings is necessary. In the case of distinct fabrication and probing scenarios, this necessity entails precise alignment steps in order to prevent misalignments regarding both incident angles in the order of $0.01^\circ$, which is impractical for compact optical systems. In the context of this paper, the extraordinary low tolerance for mechanical misalignments highlights the benefits of instantaneous alignment of the metasurface with respect to the specific application scenario, without the need for any post-process alignments.

Figure 4d emphasizes the spectral sensitivity of the device. It should however be noted, that the spectral characterization of the described phenomenon requires a sampling light source that is largely identical to the light source applied during sample preparation in terms of coherence and radiance.

However, the monochromatic probing of the metasurface also enables to address a broad range of refractive indices. For instance, the spatial variance of the effective refractive index $n_{\text{eff}}$ of the SPP mode during growth allows for a corresponding shift of the reported feature dependent on the position on the sample. Such changes of $n_{\text{eff}}$ can be introduced by a refractive index gradient in the ELD solution or even electro-optic effects of a nonlinear material close to the surface.

In summary, a light source is directed onto a sample with a fixed incident angle. This light source enables the plasmon-induced growth of a nanostructure, which is adapted to its electromagnetic environment and is therefore sensitive to minute deviations. Due to the fixed incident angle during fabrication and probing, the issue of low tolerances for mechanical misalignments is circumvented. This way, high-performance optical sensors can be achieved as compact optical systems without facing challenging, post-process alignments. This is particularly beneficial for integrated optical systems, for which we propose an on-chip light source (e.g., a laser diode) with a fixed incident angle with respect to the chip's surface. The light, which is reflected at this surface, is detected by an on-chip detector (e.g., a photo diode). In the context of this study, a metasurface-based integrated optical device, which commonly requires multiple-step, complex fabrication methods, can then be realized from the petri-dish.

3. Conclusion

We have shown instantaneous disorder engineering of a plasmonic metasurface based on AgNPs, using a plasmon-induced deposition technique. After the deposition, this metasurface is inherently sensitive towards changes in the EM environment relative to the conditions during the growth. While a high sensitivity to changes in the EM environment commonly yields a low tolerance for mechanical misalignments, the resulting metasurfaces are here intrinsically aligned to the specific wavefronts of a fixed light source, which was used for the plasmon-induced growth. The resulting high sensing performance of the system is governed only by the laser’s divergence. Thus, to obtain higher sensing performances, only a more parallel laser beam is required.

Because of its versatility (photonic and plasmonic platforms) in combination with facile fabrication and high performance, the approach reported in this paper is foreseen as initiating a shift of focus towards cost- and labor-efficient, bottom-up fabrication methods in the field of functional metasurfaces.

Further, controlling the plasmon-induced growth of metasurfaces, via tuning of excitation schemes and growth parameters, enables in-situ k-space engineering of metasurfaces. We believe that this approach will pave the way for applications of metasurfaces with tailored optical response within low-cost integrated optical systems beyond optical sensors.

4. Experimental Section

Sample Fabrication: Sapphire chips of thickness $t = 500 \mu\text{m}$ serve as substrates for the experiments. On top of the sapphire, an ultrathin chromium film ($t = 1.5 \text{ nm}$) was deposited as adhesion layer, followed by a silver film ($t = 54 \text{ nm}$) was deposited by thermal evaporation. Afterwards, a poly(methyl methacrylate) (PMMA) film ($t = 15 \text{ nm}$) was spin-coated on top of the silver film. This PMMA film serves as a buffer, which enables particle formation on top of the PMMA film instead of film growth of the silver during the process. The film thicknesses were measured using a profilometer (Dektak 3ST). The AgNPs were grown from solution using the electroless deposition (ELD) technique. This deposition technique, published elsewhere,[25] was slightly modified with respect to the solutions’ ammonia content (18.5 wt%) to reduce the growth rate of AgNPs. An excitation of SPPs propagating along the Ag/PMMA interface was implemented in a Kretschmann configuration using a diode laser ($\lambda = 660 \text{ nm}$, $P = 70 \text{ mW}$) and a semi-cylindrical sapphire prism. First, the laser beam was p-polarized using a linear polarizer, then the incident angle was set corresponding to the SPP resonance conditions and thus maximized coupling of photons to SPPs. To initiate the deposition step, the water-based ELD solution was drop cast on top of the sample at the position of maximum optical power density ($I_{\text{max}} = 0.2 \text{ W cm}^{-2}$). During the deposition, the reflected optical power was monitored using a photodiode-based optical power meter (Thorlabs S151C).

Optical Probing: After the removal of the ELD solution, the samples were stored under ambient conditions. Within the duration of the experiments of more than 1 year, no alteration of the morphology of the samples was observed. For optical probing, the flow cell attached to the sample is filled with water ($n_w = 1.333$). Then the RI of the analyte is continuously tuned by adding ethanol ($n_a = 1.364$) to the water via an external reservoir, which is connected to the flow cell. This way, the accessible range of the RI includes the dielectric properties of the water-based ELD solution ($n_w < n_{\text{ELD}} < n_a$) and thus also covers the growth conditions. During the change of the analyte, the reflectance of the metasurface in the Kretschmann configuration is measured using the same optical power meter that was used during the deposition.

Scanning Electron Microscopy: The SEM investigations were conducted using a Philips XL30S FEG system with a field emission cathode.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.
Acknowledgements
This project has received funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation program (Grant Agreement No. 637367).
Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
engineered disorder, k-space engineering, metasurfaces, nanoparticles, plasmonics, self-alignment

Received: January 28, 2022
Revised: February 11, 2022
Published online: March 13, 2022

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