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0.1 Coupling Nanodiamonds to Double Bowtie Antenna Structures

Plasmonic nanoantennas are very recent devices designed to efficiently convert freely propagating optical radiation into localized energy and vice versa [?, ?, ?, ?, ?, ?]. Leveraging this unique property, integrating SiV centers with optical antennas creates coupled systems with a range of desirable features. These include enhanced photoluminescence emission and the ability to tailor photoluminescence spectra of the integrated emitters. The latter can be achieved by tuning the physical design parameters of the system including antenna geometry and emitter placement.

In this chapter we report on our efforts aimed at enhancing the properties of SiV centers by coupling them to optical double bowtie antennas. To this end we transfer selected nanodiamonds containing SiV centers to the target antenna structure using pick-and-place methods. After successful coupling we investigate the integrated structure experimentally. In addition to that we successfully relate some of our results to theoretical predictions.

In the following we give a short discussion of the most important properties of optical antennas. Then we sketch the actual coupling process and report on the optical properties of the resulting integrated structure. To our knowledge, our experiments were the first attempts of coupling SiV centers to plasmonic bowtie antennas.

0.1.1 Plasmonic Antennas

Optical nanoantennas act as converters between propagating and localized electro-magnetic fields. Thus, they can be used efficiently to couple photons in and out of nanoscale objects [?]. Due to their small physical sizes, comparable or smaller than the wavelength of visible light, they are capable of focusing optical fields to subdiffraction-limited volumes, offering the ability to manipulate electromagnetic fields at nanoscales [?, ?]. This property, dubbed sub-wavelength confinement, has successfully been exploited to enhance the excitation and emission of quantum emitters [?, ?, ?, ?] and to modify their spectra [?]. Resulting practical applications include near-field optical microscopy [?], surface enhanced spectroscopy [?, ?] and molecular sensing [?].

A nanoantenna is a nanostructure made from materials such as noble metals like gold or silver. These metals have in common that they are very susceptible to being polarized by electromagnetic fields. When illuminated by the incident electromagnetic radiation causes electrons in the metal to behave as a plasma that tends to move with respect to the atomic lattice. As a result excess charge at the opposite surfaces of the material accumulates and the material becomes temporarily polarized until restoring forces equilibrate the charge distribution.

Thus incident light of a given frequency induces oscillations in the free electron gas density in the surface layers of the metal. At resonance these light-induced oscillations exhibit modes of standing waves. The quasi-particles associated with these modes are known as localized surface plasmons (LSPs). For an in-depth treatment of LSPs in the context of nanoantennas we refer the reader to [?] and references therein.

Here it suffices to say, that LSPs facilitate the deciding property of optical antennas: Converting electromagnetic energy from the far-field into localized energy in the near-field. This

allows, in combination with the high collection-efficiencies of nanoantennas, to efficiently couple visible radiation with wavelengths of hundreds of nanometers, into small effective spatial volumes of only a few nanometer in diameter.

To create a controlled hot-spot several antenna designs are possible. In the context of this thesis we rely on double bowtie antennas available via a collaboration with N. Rahbany, group of C. Couteau, University of Technology of Troyes. Figure 1 illustrates the typical bowtie antenna.

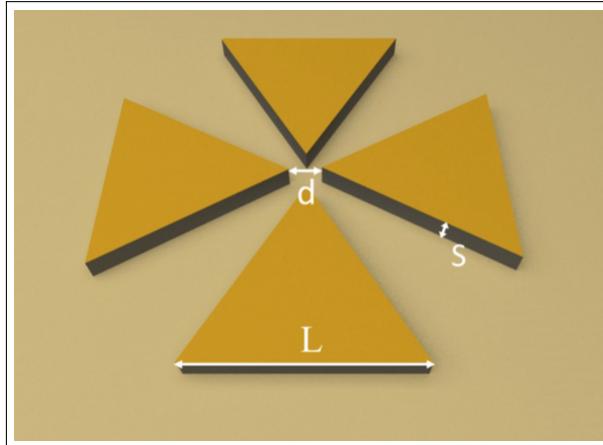


Figure 1: Schematic of a double bowtie antenna [?, ?, ?].

This antenna design utilizing a symmetric arrangement of four identical triangle-shaped blocks, separated by a small gap. This setup allows LSP modes local to individual blocks to couple with each other resulting in the formation of an intense hot-spot in the center area [?], see ?. The actual electromagnetic response of a double bowtie nanoantenna depends on its physical design parameters such as gap size, material used, geometry and size. Furthermore, properties of incident light such as wavelength and polarization determine antenna operation.

The improved electromagnetic field at the center of a metallic nanoantenna can be used to increase the spontaneous emission rate of emitters emitting at frequencies close to the resonance frequency of the antenna. This result is the known as Purcell effect [?]. The gap between the antenna arms acts as a resonant cavity providing a strong near field interaction with the emitter. This interaction modifies the density of states of the system, effectively providing additional modes for the emitter to decay into, thus amplifying its total decay rate. The amplification affects both radiative and non-radiative decay. The magnitude of the amplification for an emitter is quantified by the ratio of its enhanced decay rate to its free space decay rate, known as the Purcell factor F_p . This factor is proportional to Q/V_{eff} where Q denotes the quality of the antenna and V_{eff} the volume of the hot-spot. Thus antenna design must optimize F_p as a necessary condition for significant enhancement of fluorescence light emission.

In addition to the antennas local field enhancement, the emitters original quantum yield η_0 influences the overall effectiveness of the emission enhancement. From theoretical considerations [?, ?, ?, ?], the modified quantum efficiency η of the combined system consisting of

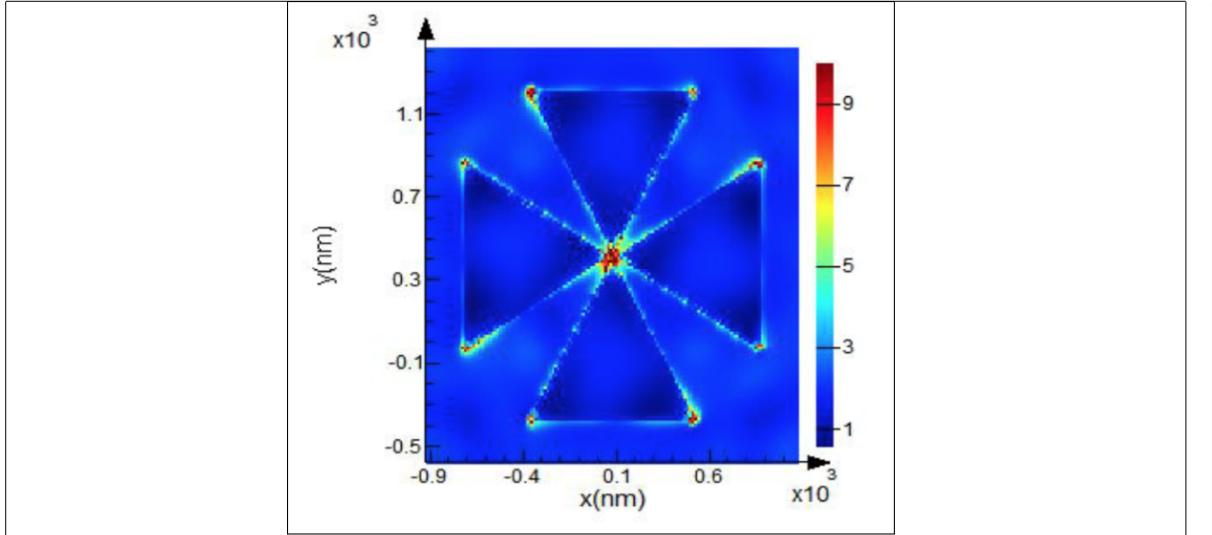


Figure 2: Simulation result of the electric field map of a gold double bowtie nanoantenna [?, ?, ?]. The structure has gap of $d = 150$ nm, a side length of $L = 2\text{ }\mu\text{m}$ and a thickness of $S = 60$ nm. The center of the antenna exhibits an area of pronounced focus, the so-called hot-spot.

emitter and antenna can be obtained as

$$\eta = \frac{\eta_0}{\frac{1-\eta_0}{F_p} + \frac{\eta_0}{\eta_{ant}}}, \quad (1)$$

where η_{ant} denotes the fraction of fluorescence light which is not dissipated through losses in the metal of the antenna. It is clear that an emitter with $\eta_0 \rightarrow 1$ will not profit from the Purcell effect. On the contrary, for realistic antennas with $\eta_{ant} < 1$ antenna-induced losses reduce the overall quantum yield η . Consequently poor emitters with low initial η_0 stand to profit the most from antenna-emitter coupling provided antennas are engineered well, i.e. they maximize their Purcell Factors and minimize their losses. For an in-depth review

The presented considerations illustrate that due to their relatively low quantum efficiency, SiV centers are excellent candidates for coupling with antennas. Thus it is promising to exploit the improved electromagnetic field at the center of a double bowtie antenna to enhance the spontaneous emission rate of SiV centers and thus improve their merit as single photon sources.

0.1.2 Plasmonic Antenna Design and Simulation

To couple SiV centers to optical antennas, we work with gold double bowtie antennas on a gold substrate. In comparison with triangular, or single bowtie antennas, double bowtie antennas offer significantly improved intensity enhancements. Antennas were provided by N. Rahbany, group of C. Couteau, University of Technology of Troyes in a joined effort to explore the possibilities of combining antennas with SiV centers. The antennas themselves were fabricated using electron beam lithography, a technique suitable to imprint predetermined patterns onto a suitable substrate with nanoscale resolution [?]. Figure 3a shows a SEM image

of an array of antenna structures of various sizes. In Figure 3b a detail of an individual double bowtie antenna is shown. It can be seen that the double bowtie antenna is placed in the center of another structure, a so-called bulls-eye antenna, consisting of multiple concentric gratings. When illuminated by a laser at a proper angle, the gratings excite surface plasmon polaritons (SPPs) which are directed towards the center of the structure. If a double bowtie antenna is present in the center, SPPs can interact with the LSPs of the double bow tie, leading to an even stronger localization of electromagnetic fields in the gap of the bowtie. While this interaction certainly merits exploration in the context of enhancing SiV centers, we omit the excitation of SPPs in our first exploration of the coupling of SiV centers and antennas. Thus the presence of the gratings can be ignored for our purposes. The reader interested in the details of bulls-eye antennas and their properties is referred to [?].

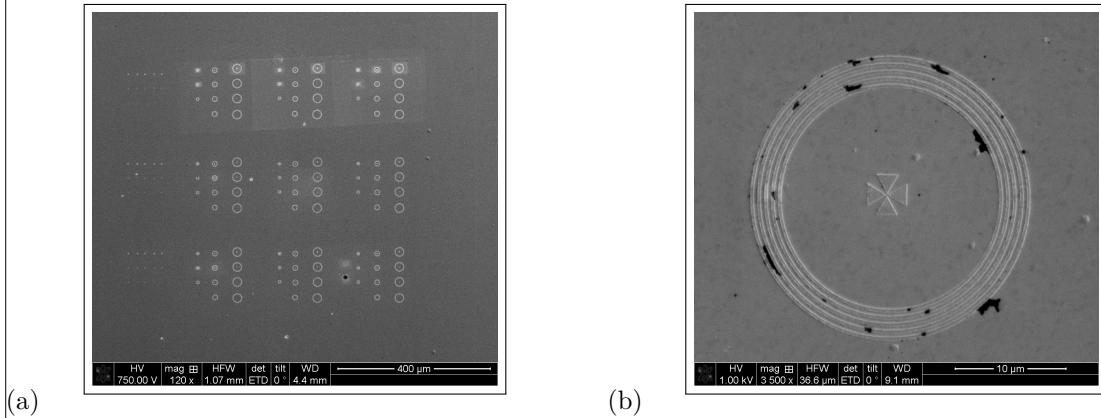


Figure 3: SEM images of antenna structures. (a) Overview of a field of antenna structures exhibiting various dimensions. (b) Detail of one antenna structure. In the middle the double bowtie design is visible. A grating structure consisting of multiple gratings is surrounding it.

To effectively enhance the emission of an emitter by coupling it to an optical antenna, the emission wavelength must match the resonant wavelength of the antenna. In the context of SiV centers a value of 738 nm is required. Since this value can be considered constant, the design parameters of the antenna must be chosen such, that the resulting resonance matches it. An additional constraint is placed on the size of the antenna gap, since it must be big enough to accommodate nanodiamonds hosting SiV centers, the former are around 100 nm in size. However, it cannot be chosen arbitrarily big, since bigger gaps lead to larger effective volumes and thus smaller Purcell Factors.

Using finite difference time domain (FDTD) simulation deploying Lumerical Software the design space of gold double bowtie nanoantennas on a gold substrate was explored [?]. Although we initially attempted to simulate antennas without a nanodiamond present in the gap, it was subsequently discovered that its ab initio inclusion yielded superior results. Thus to determine usable design parameters for our purposes, an integrated system combining antenna and nanodiamond was used. To better mimic experimental conditions and associated imperfections, the nanodiamond was placed slightly off-center in the gap.

In a series of simulations it was established that a gap size of $d = 150$ nm, a side length of $L = 2$ μm and a structure thickness of $S = 60$ nm are feasible parameters as referred to in [?]. The simulation required the index of refraction for gold which was taken from Palik [?, ?, ?, ?].

The resulting geometry hosting a nanodiamond is capable of producing a suitable hotspot when excited.

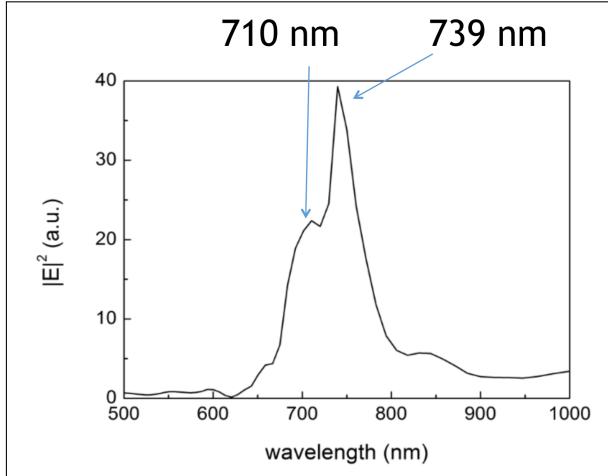


Figure 4: FDTD simulation of the electric field intensity of a double bowtie nanoantenna as a function of the wavelength of incident light. Two peaks are identified. The major peak corresponds exceptionally well with SiV center emission at 738 nm. The minor peak is attributed to the presence of a nanodiamond.

Finally, to pin-point the resonant wavelength for the antenna hosting a nanodiamond, the electric field intensity is simulated as a function of the wavelength of the incident light. The resulting spectrum is shown in Figure 4. Two resonant peaks are found. The intense major peak at 739 nm coincides exceptionally well with the SiV center emission wavelength 738 nm indicating successful antenna design. In addition to the major peak, an additional minor mode at a lower wavelength of 710 nm is found [?]. We remark that if the nanodiamond in the gap of the antenna is removed from the simulations, the minor feature vanishes. Thus the additional peak is well-attributed to the presence of the nanodiamond.

In summary, the combined simulation results suggest, that the engineered system of nanoantenna and nanodiamond is well suited to effectively enhance the emission from an SiV center hosted in the nanodiamond. In the following sections we report on the experimental realization of this preposition.

0.1.3 SiV center in a Plasmonic Double Bowtie Antenna

In the following we report on our attempts to couple SiV centers to gold double bowtie nanoantennas in order to study the properties of the resulting integrated system. Ideally, a suitable nanodiamond containing exactly one SiV center is placed in the center of the antenna. The term suitable is used to summarize both desirable spectroscopic properties such as narrow-bandwidth saturated single-photon emission as well as technical requirements such as nanodiamond size and degree of isolation on the surface. Naturally, the odds of identifying and addressing a nanodiamond fulfilling all these criteria simultaneously are small. As a result identifying a perfect candidate for coupling is prohibitively time-consuming.

To mitigate this difficulty we decided to relax the condition of exactly one SiV center per

nanodiamond and initiate our explorative work with nanodiamonds containing several, potentially many active SiV centers. Relying on $g^{(2)}(0)$ measurements we identify two interesting classes of nanodiamonds. The first class consists of nanodiamonds containing large ensembles of SiV centers acting as coherent emitters. The fluorescence light received from large ensemble of emitters is mainly coherent, leading to a flat response in the $g^{(2)}(0)$ function. The second class of nanodiamonds we investigate features nanodiamonds hosting multiple SiV centers. As a result relevant $g^{(2)}(0)$ measurements report weak but discernable anti-bunching dips. Both classes have in common that relevant nanodiamond specimen are significantly easier to obtain than nanodiamonds containing singleton SiV centers. Thus nanodiamonds containing ensembles of SiV centers as well as nanodiamonds containing few SiV centers are both valid starting points for our work. It is likely that the experience gained during our preliminary explorations will be valuable once nanodiamonds containing singleton SiV centers become available.

In the following sections we report on our efforts to couple nanodiamonds containing SiV centers to antennas. We illustrate the coupling process and its challenges and discuss relevant results regarding the coupling of nanodiamonds of the classes described above. We close the chapter with a short discussion and suggestions for further research.

Nanodiamonds Containing Ensembles of SiV centers Coupled to Antennas

Remark:

- fuer Figure 6b braucht noch das richtige bild. also eine g2 function mit coherent light
- die photostrecke pick-and-place kannst du noch nancy bilder durch deine Bilder ersetzen. Ansosten muessen da noch nancy citate hin.

The nanodiamonds used for the approach of coupling ensembles of SiV centers to an antenna were wet-milled from a CVD diamond film¹. The solution of nanodiamonds exhibiting a median size of 100 nm was spin-coated on an iridium substrate treated with Piranha etch. To ensure that a pre-selected nanodiamond exhibiting preferred optical properties can reliably be located, the iridium substrate was engraved with reference cross markers produced by a focused ion beam after the spin-coating process. After spin-coating, the sample was placed in an oven for 3 h at 450 °C to oxidize the surface and remove any residual graphite and amorphous carbon. See ?? for more information.

To determine the position of nanodiamonds on the original substrate, first a scan with a commercial laser scanning microscope (LSM) was performed as described in ???. Figure 5a shows a part of an obtained LSM image. After transferring the sample into the confocal setup, confocal fluorescence light scans of the corresponding areas are performed to identify nanodiamonds containing active emitters. The scanned area is shown in Figure 5b. It corresponds to the area shaded blue in Figure 5a. Thus, upon close inspection some of the bright spots appearing in the fluorescence light scan can be associated with selected nanodiamonds in Figure 5a by eye. The correspondence between the SEM and LSM images in conjunction with the cross-markers on the substrates allows to precisely locate preselected nanodiamonds

¹wet-milling performed by A. Muzha, group of A. Krueger, Julius-Maximilians Universität Würzburg, diamond film grown by group of O. Williams, School of Engineering, Cardiff University

containing suitable emitter in the SEM.

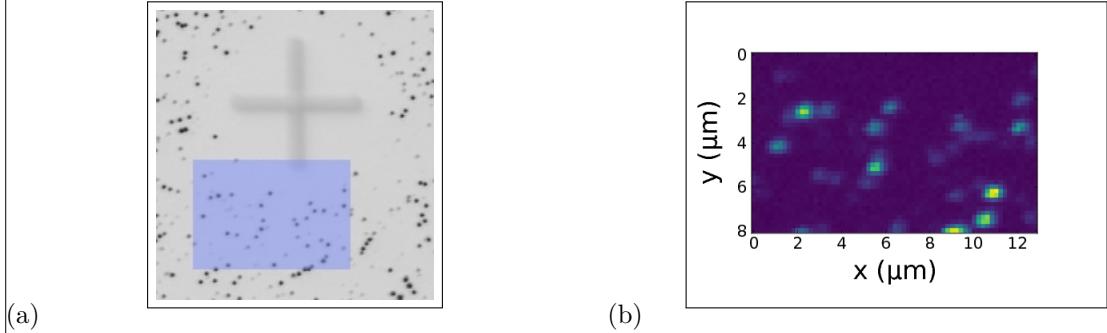


Figure 5: (a) Picture recorded with a commercial high resolution laser scanning microscope. Black dots are individual nanodiamonds. The cross-marker serves as an orientation aid. The area shaded in blue represents the photoluminescence scan in image (b). (b) Photoluminescence scan of a $8 \mu\text{m} \times 13 \mu\text{m}$.

The most promising candidate nanodiamonds are characterized by fluorescence light spectra with very narrow zero-phonon-lines and minimal phonon side band features. Figure 6a shows the spectrum stemming from one such preselected nanodiamond. The ZPL feature exhibits a center wavelength of (738.55 ± 0.01) nm and a linewidth of (5.00 ± 0.03) nm, corresponding well with the ZPL of unstrained SiV centers. Photon autocorrelation measurements revealed that the nanodiamond contains an ensemble of SiV centers collectively generating coherent fluorescence light light, see Figure 6b.

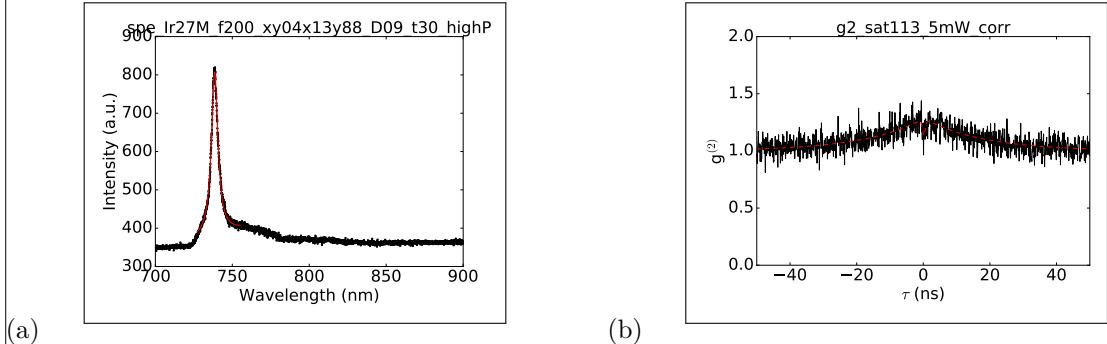


Figure 6: a) PL spectrum of the emitter in the preselected nanodiamond at room temperature. Black: experimental results; red: fit to experimental data, which yields a ZPL center wavelength of (738.55 ± 0.01) nm and a linewidth of (5.00 ± 0.03) nm. b) Intensity autocorrelation function recorded for the ensemble of emitters hosted by the nanodiamond. The flat response indicates the coherent nature of the fluorescence light light.

After a proper candidate for coupling with an antenna has been identified, it needs to be relocated from its original substrate to the antenna. To this end a pick-and-place process introduced in ?? is used. A complete illustration of the steps involved is given in Figure 7.

We remark that the gold surface of the plasmonic antenna exhibited strong adhesion forces between the antenna surface and the nanodiamond. Once the nanodiamond touched the gold, it could not be picked up again with the tungsten tip. The nanodiamond first touched the antenna structure a few nanometers away from the gap and immediately stuck to the

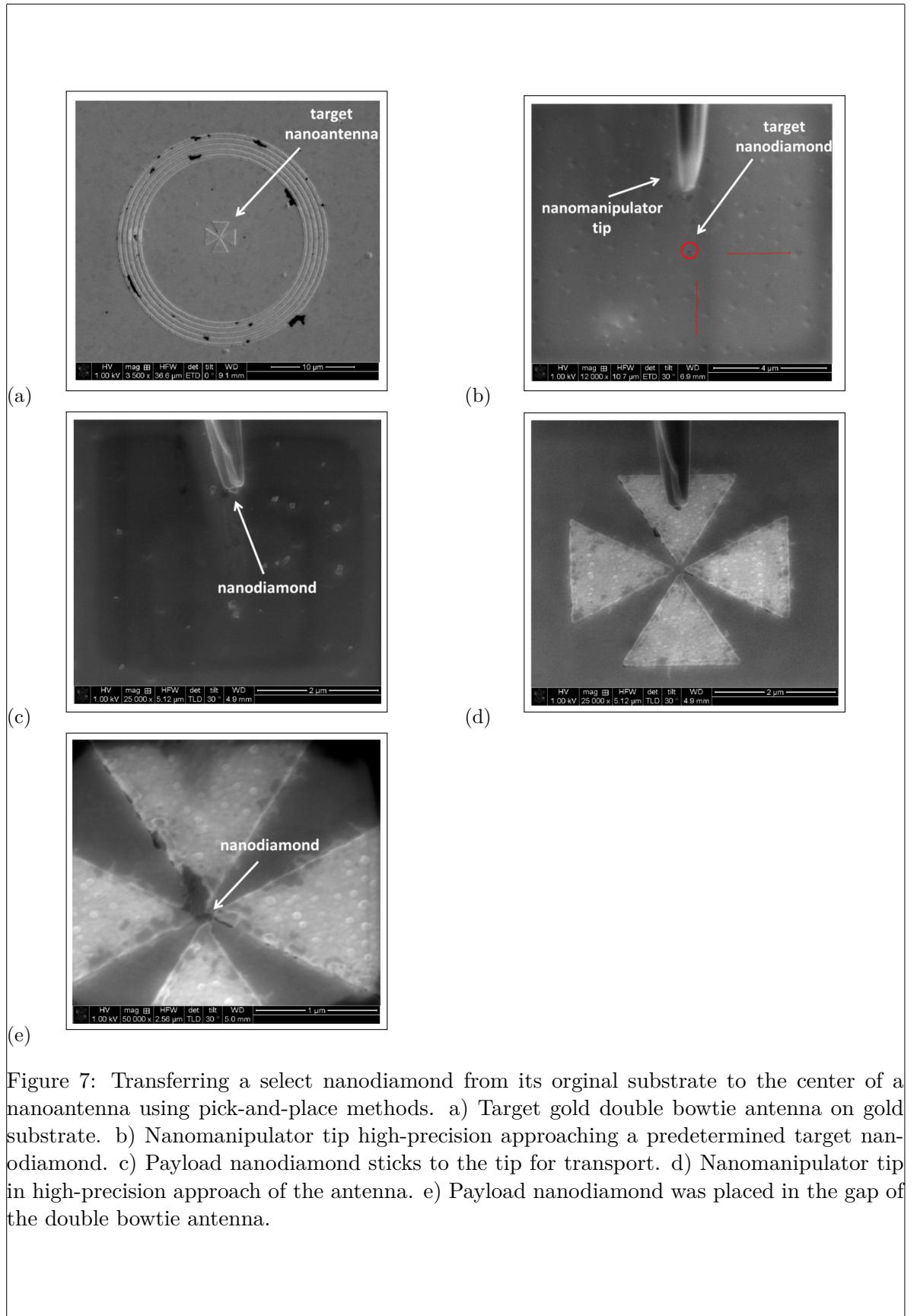


Figure 7: Transferring a select nanodiamond from its original substrate to the center of a nanoantenna using pick-and-place methods. a) Target gold double bowtie antenna on gold substrate. b) Nanomanipulator tip high-precision approaching a predetermined target nanodiamond. c) Payload nanodiamond sticks to the tip for transport. d) Nanomanipulator tip in high-precision approach of the antenna. e) Payload nanodiamond was placed in the gap of the double bowtie antenna.

surface, on top of one of the triangles. Therefore, the nanodiamond had to be pushed into the gap with the nanomanipulator tip. This process caused some damage to the antenna structure. The damage is visible as black area at the tip of the top triangle in Figure 7e. Luckily, FDTD simulations of damaged antennas reveal that this modification of the antenna hardly influences the antenna resonance.

After successful placement, the antenna sample is installed in the confocal setup. The antenna itself was located during a scan of the sample surface under white light illumination. A scan of the antenna is performed in the confocal setup using a 660 nm continuous wave laser. It serves to locate the middle of the antenna structure and therefore the nanodiamond which had been placed there. An outline of the rings is visible in an overview scan of the antenna structure shown in Figure 8a. Zooming in to the exact center of the rings, some of the edges of the bowtie antenna are vaguely visible in Figure 8b.

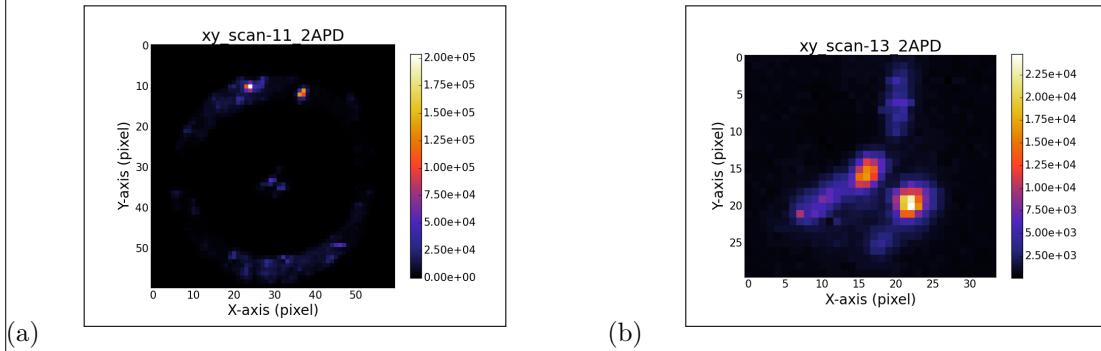


Figure 8: (a) Confocal scan of the double bowtie antenna where a nanodiamond containing multiple SiV centers had been placed. The rings are visible. (b) Detail scan of the triangles of the same antenna structure, which make up the double bowtie antenna. While the separate triangle cannot be seen, some edges and two bright spots are visible. To identify the place of the nanodiamond we compare the middle point of the rings in (a), the point of intersection of the edges and the bright spot and conclude that the upper bright spot in (b) is the location of the nanodiamond.

These images suffice to locate the nanodiamond with sufficient precision to measure PL spectra. The PL spectrum of the ensemble of SiV centers in the nanodiamond is shown in Figure 9a. It can be seen that at 738 nm a major peak is present, almost exactly at the same wavelength than the SiV center zero-phonon-line, i.e. 739 nm. The additional minor peak at 726 nm is attributed to the antenna resonance mode. We remark that, any damage sustained through electron radiation during the pick-and-place process is likely not sufficient to invalidate the nanodiamond. This is expected as a large ensemble of SiV centers can easily lose several emitters without any noticeable difference in the optical properties. Needless to say, the exact opposite is true for nanodiamonds with very few hosted SiV centers making them risky to work with.

We verified successful coupling of the ensemble of SiV centers to the antenna by combining experimental and numerical results. In particular, we convolve the experimental PL spectrum of the nanodiamond measured before placing it in the nanoantenna, see Figure 6a, with the intensity spectrum of the nanoantenna obtained by means of simulations given in ???. The result of the convolution is the spectrum given in Figure 9b. The agreement with the measured spectrum in Figure 9a is almost perfect, indicating successful coupling of emitters

and antenna. At the same time we confirm that the minor peak in Figure 9a is indeed due to the antenna resonance.

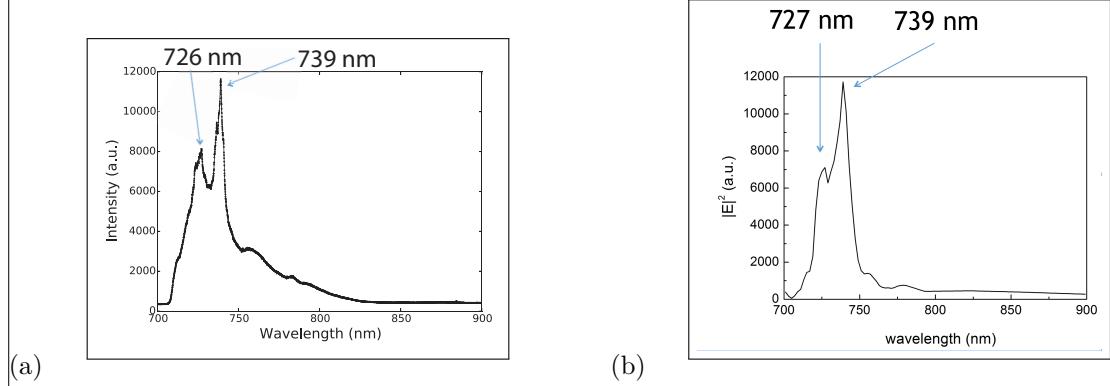


Figure 9: (a) Measured PL spectrum of the emitter after placing the nanodiamond into the nanoantenna, (b) Convolution of the spectrum of the measured PL spectrum of the emitter before pick-and-place, see Figure 6a, and the simulated resonance spectrum of the nanoantenna, see Figure 9a.

Finally, keeping experimental conditions unchanged, we measure a spectrum of an identical antenna without a nanodiamond present in order to rule out surprising artifacts induced by the antenna itself. The resulting spectrum is given in Figure 10.

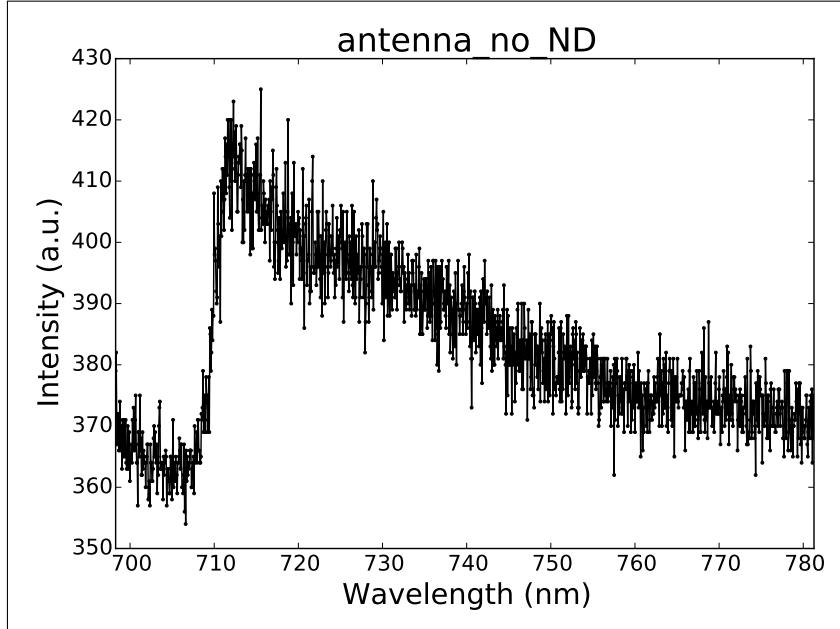


Figure 10: Spectrum of a gold double bowtie nanoantenna without a nanodiamond present.

At this point one must resist the temptation of comparing the values of the intensity maxima of the spectra in Figure 6a and Figure 9a in order to determine the enhancement the ensemble of emitters experiences. These values inherently do not allow a meaningful comparison.

A meaningful comparison can in principle be achieved via intensity saturation measurements.

By measuring the saturation intensities before and after insertion into the antenna and accounting for effects related to the polarisation of emitters, the magnitude of the Purcell enhancement can be determined. Unfortunately, these methods are reserved for single emitters and do not apply for ensembles of SiV centers. Thus at this point we have no method to determine the Purcell enhancement ensembles of SiV centers experience.

In summary, in this section we showed that coupling of nanodiamonds containing ensembles of SiV centers with gold double bowtie antennas is feasible using a pick-and-place approach. Furthermore we verified that the coupling is indeed present after the nanodiamond was placed in the gap of the antenna. Unfortunately, at present there is no reliable method available to us to quantify the magnitude of fluorescence light enhancement experienced by the SiV center ensemble.

Nanodiamonds Containing Few SiV centers Coupled to Antennas

Remark:

- FDTD bilder fehlen komplett. Muessen unten eingefuegt werden.
- FDTD simulation fuer verschiedenen dipole orientations werden kurz erwähnt, gibts da bilder?
- Fuer das spectrum von nanodiamond + antenne sind die locations von den subpeaks wichtig? Irgendwo sollte erwähnt werden, dass der neue major peak nicht dort ist wo man die SiV center zero-phonon-line erwarten würde.
- Die fits an die subpeaks von dem spectrum nanodiamond + antenne werden nicht erklärt. Wenn die nicht wichtig sind, sollte man sie zumindest beiläufig erwähnen.

After a first successful validation of inserting nanodiamonds hosting large ensembles of SiV centers into a gold double bowtie antenna, we attempt to select nanodiamonds containing a comparatively small number of SiV centers. Suitable nanodiamonds show an anti-bunching dip in the $g^{(2)}$ function in addition to countrate saturation. This can be regarded an intermediate step towards using nanodiamonds containing singleton SiV centers. We stress that in comparison to nanodiamonds hosting large ensembles of emitters, nanodiamonds containing only a few emitters are already difficult to identify. Naturally, technical requirements applying to candidate nanodiamonds such as sufficient isolation for picking it up in the pick-and-place process and a size not larger than that of the antenna gap still need to be observed.

The starting material for the nanodiamonds used here was an electronic grade diamond film produced by the company rho-BeSt coating (now renamed to CarbonCompetence). The film was then milled in a bead-assisted sonic disintegration process² to nanodiamonds of a median size of approximately 100 nm. The nanodiamonds were drop-cast at 60 °C onto an iridium substrate containing cross markers. Prior to drop-casting the substrate was cleaned with Piranha etch.

Given samples containing nanodiamonds the tedious task of identifying potential candidates for transfer to the antenna. As described in the previous section, a commercial laser scanning microscope (LSM) is used to identify nanodiamonds on the substrate. Using the cross markers

²A. Krueger, Julius-Maximilians Universität Würzburg

to address their exact positions, a corresponding fluorescence light scan allow us to single out nanodiamonds with bright emission. We further test the suitability of potential candidates as follows. First, a saturation curve is recorded to establish whether the SiV centers in a nanodiamond saturate. Since saturation is a necessary albeit not sufficient condition for single-photon emission, only nanodiamonds that saturate are capable of showing an anti-bunching dip in the $g^{(2)}$ function. Note that, measuring the $g^{(2)}$ function potentially requires hour-long measurements, while determining saturation requires merely seconds. Thus, in search of candidate nanodiamonds we may use the saturation behaviour as a quick check whether a candidate is feasible to follow up with a lengthy $g^{(2)}$ function measurement. For nanodiamonds containing SiV centers showing saturation we then check the spectrum to assert that the emitters are indeed SiV centers. After this last check $g^{(2)}$ function measurements are established.

After a significant search, involving a sizeable number of discarded candidates, a nanodiamond with a discernable anti-bunching dip was found. ?? shows its $g^{(2)}$ function function while Figure 11b reports its saturation curve. While the dip in $g^{(2)}$ function is quite weak, it is present and a fitting it was possible. This indicates that the nanodiamond neither contains a singleton SiV center nor does it host enough SiV centers to emit coherent light. Thus we conclude that a limited number of SiV centers must be present. While it is not possible to quantify the number of emitters directly, the candidate sufficiently differs from nanodiamonds hosting large ensembles of SiV centers. Thus it is viable to take it to the stage of coupling.

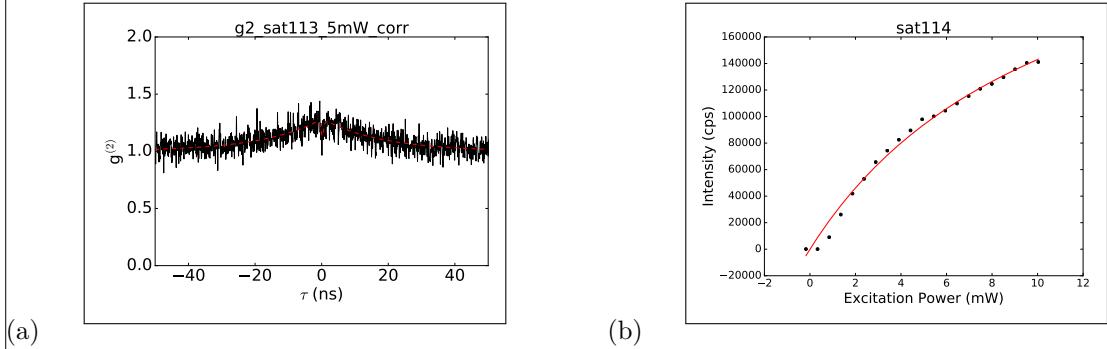


Figure 11: (a) The $g^{(2)}$ function of the preselected nanodiamond believed to host a limited number of SiV centers. A dip at $g^{(2)}(0)$ is present, however its decrease is not sufficient for a singelton SiV center. This indicates that a limited number of SiV centers is present since the absence of a dip can only be measured under coherent emission, i.e. for larger ensembles of SiV centers. The dashed red line gives a fit to the data.

cps zu a.u. aendern

. (b) Saturation curve of the same emitter

zahlen fuer sat eintragen

. Data points are black, fitted curve red.

In order to relocate the identified nanodiamond to the center of a gold double bowtie antenna we repeat the pick-and-place procedure described in the previous section, see Figure 7. We remark at this point that since the nanodiamond in question contains fewer SiV centers as compared to the nanodiamonds hosting large ensembles of SiV centers, it is expected to be less resilient to adverse effects such as the electron radiation present during the pick-and-place

process.

After a successful relocation, the sample containing the antenna is mounted in the confocal setup to investigate the properties of the combined system consisting of antenna and SiV centers. Figure 12a gives the spectrum of the candidate nanodiamond after being relocated to the center of a gold double bowtie antenna. Interestingly we find a multitude of individual peaks in the vicinity of the SiV center zero-phonon-line line. In addition we find that the sideband appears more pronounced in relation to the intensity of the major feature after the nanodiamond has been relocated to the antenna. Due to the shape of the recorded sideband we conjecture that it arises as a combination of the phonon side bands associated with individual SiV centers and additional contributions due to fluorescent contaminations. Figure 12b showing the spectrum of the same nanodiamond before being relocated to the antenna. Here the phonon side band is weaker in comparison to the zero-phonon-line feature.

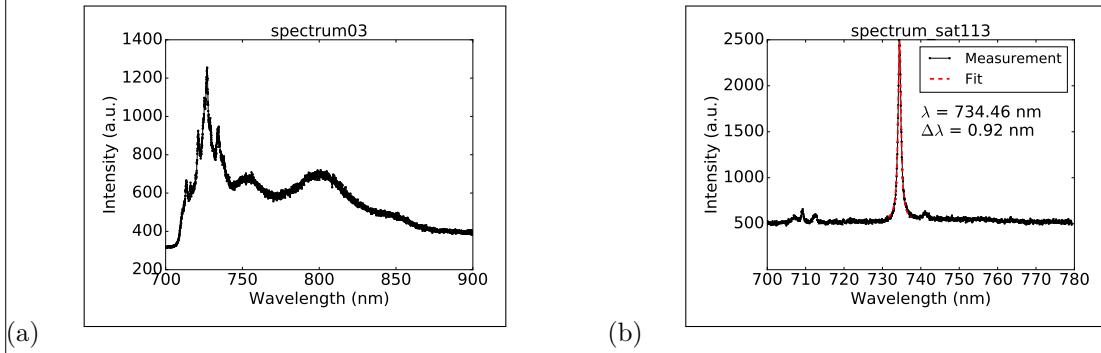


Figure 12: (a) Spectrum of the preselected nanodiamond hosting few SiV centers after being relocated to the center of a double bowtie antenna. (b) Spectrum of the same nanodiamond before relocation.

To exclude the possibility that the obtained peaks are artifacts due to misalignment of the experimental setup, we rechecked the alignment which proved to be precise.

To reverify the obtained spectrum, we repeated the measurement. Unfortunately, we obtained an entirely different result, showing only a broad background seen in Figure 13a. After checking in the confocal scan that the measurement was performed at the correct position, we had to conclude that all of the SiV centers hosted by the nanodiamond permanently bleached after recording the spectrum seen in Figure 12a. It is likely that continued application of energy from the laser triggered this effect as earlier independent measurements established that SiV centers exhibit an increased likelihood of bleaching after being exposed to electron radiation [6]. Thus we conclude that the exposure to electron radiation during the pick-and-place left the SiV centers in an unstable state susceptible to bleaching.

Even though the nanodiamond was invalidated for further measurements, the spectrum that was obtained remains to be discussed further. To better understand the obtained observations, we turn to FDTD calculations of nanodiamond coupled to a gold plasmonic double bowtie antenna as described in the beginning of this chapter. In particular, we fold the spectrum of the nanodiamond before insertion into the antenna as given in Figure 12b with the simulation spectrum of the integrated system consisting of nanodiamond and antenna. The simulation result thus constitutes a prediction of what the spectrum in Figure 12a should look like. ?? illustrates the simulation prediction and demonstrates that we have no reason

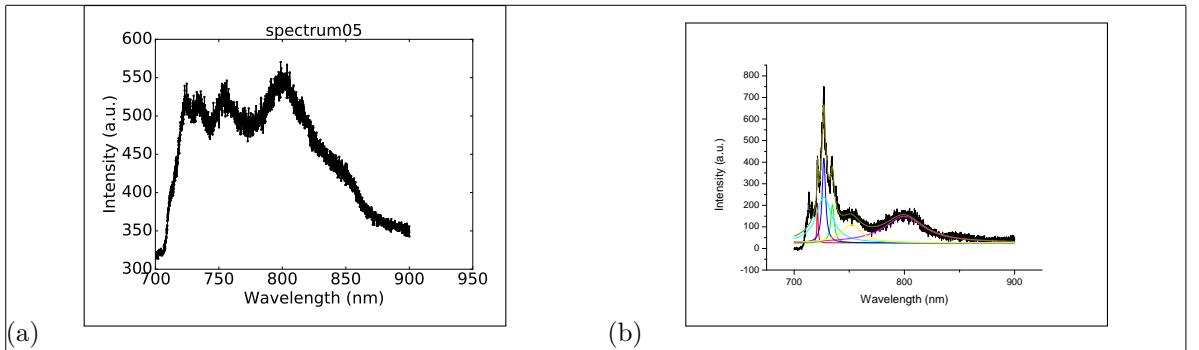


Figure 13: (a) Spectrum of the nanodiamond hosting few SiV centers coupled to the double bowtie antenna after the emitter bleached. (b) Background corrected spectrum of the transferred nanodiamond in the double bowtie antenna. Peaks are fitted, results of the fits are the colored lines. For background correction, the spectrum in (a) was used.

to expect the to see the peaks between 700 nm to 750 nm observed experimentally. Hence we must conclude that the spectrum of the nanodiamond was modified during the pick-and-place process. While it is not possible to pinpoint exactly which circumstance caused the modification, several effects could influence the observed spectra.

First, the electron radiation itself. While it lacks the energy to modify the lattice itself, it can influence the electrons present and in particular may modify the charge state of SiV centers. As was mentioned before, electron radition was linked to increased likelihood of photobleaching.

Next, during the pick-and-place process it is possible that the nanodiamond collects additional contaminating matter on its surface. Contaminations may be florescing themselves, thus modifying the spectrum. The fact that we record a significant sideband signal in Figure 12a supports this conjecture.

Yet another property of SiV centers which should not be neglected is their dipole orientation interacting with the antenna. Conducting dedicated FDTD simulations with a focus on different dipole orientations indicated a dramatic effect on the resulting spectra. Therefore, future experiments aiming to investigate the effect of coupling nanodiamonds containing few SiV centers to antennas should include polarization measurements to experimentally quantify the impact of the emitter orientation.

As it stands, the most likely explanation of the recorded spectrum consists of a combination of the discussed effects. Since the nanodiamond bleached almost immediately no further measurements were possible. It is thus advised to reapeat the experiment hoping for a nanodiamond that manages to complete the pick-and-place process unharmed. At the moment it is not clear if this can be done, thus further investigation is required.

Outlook: Nanodiamonds with single SiV centers Coupled to Antennas

To effectivly quantify the emission enhancement provided by the plasmonic double bowtie antenna, a single SiV center is necessary. A correct measure for the emission enhancement is the saturation count rate since it is proportional to the inverse of the emitter's lifetime.

put in pictures for fdfd results and reference them

Hence, if there are two or more emitters present, photons of the individual emitters are emitted randomly, which renders a correct saturation measurement impossible. However, finding SiV centers in nanodiamonds which fulfill both spectroscopic ($g^{(2)}(0) \approx 0$, saturation, narrow ZPL spectrum) and technical (size, isolation of nanodiamonds) constraints is an extremely time-consuming process. It is a search for the needle in the haystack.

We investigated different kinds of nanodiamonds in the search of nanodiamonds exhibiting optimal spectroscopic and technical parameters. We were able to fulfill the size requirements posed by the pick-and-place process and antenna design by producing different patches of different sizes of nanodiamonds and took the ones which were best suited. We also developed a good isolation of the nanodiamonds on the substrate by treating the iridium substrate with Piranha etch and tuning the amount of diamond solution drop-casted onto the substrate. This leaves us with the need of a higher probability of exactly one SiV center per nanodiamond. Parameters which have an impact on the quantity of SiV centers per nanodiamond are the initial SiV center density in the starting material and the nanodiamond size. Once the time constraint of finding a single SiV center in a nanodiamond is overcome, we can apply the extensive methods and knowledge gained by the reported procedures to couple a single SiV center to a plasmonic bowtie antenna.

To our knowledge, our experiments were the first attempts of coupling SiV centers to plasmonic bowtie antennas. The extraordinarily precise correlation of the theoretically predicted and the experimentally recorded spectrum of an ensemble of SiV centers in a nanodiamond make this process a promising candidate for future applications.