Fluorescence enhancement of a single nanodiamond with SiV centers using a plasmonic nanoantenna

N. Rahbany[1], S. Lindner[2], C. Pauly[2], D. Legrand[1], M. Atature?, R. Bachelot[1], C. Becher[2] and C. Couteau[1,3,4]

[1] Laboratory of Nanotechnology, Instrumentation and Optics, ICD CNRS UMR 6281, University of Technology of Troyes, 10000, Troyes, France

[2] ~~FR 7.2 (Experimentalphysik)~~Fachrichtung Physik, Universität des Saarlandes, Campus E2.6, D-66123 Saarbrücken, Germany

[3] CINTRA CNRS-Thales-NTU, UMI 3288, Research Techno Plaza, 50 Nanyang Drive, Singapore

[4] Centre for Disruptive Photonics Technologies (CDPT), Nanyang Technological University, Singapore

I. Introduction

Color centers in diamond are being widely used as efficient single photon sources due to their indistinguishability and photostability at room temperature. This allows them to play an important role in the fields of quantum information processing[1,2], super-resolution microscopy[3,4], and biological imaging[5]. Silicon vacancy (SiV) centers in diamond have shown to have several advantages over other types of defects due to their strong narrow fluorescence spectrum at room temperature (full width at half maximum (*FWHM*) ~~–~~< *5 nm* at *737 nm*) with low phonon coupling, a short lifetime (*1.8 ns*), and an almost fully linearly polarized zero phonon line fluorescence[6,7].

However, the reported values of the photoluminescence (PL) and radiative quantum efficiency of SiV centers so far remain low. Consequently, experiments involving coupling SiV centers to optical cavities have led to an improvement in their radiative quantum efficiency and Purcell factor, as well as a reduction in lifetime[8]. Plasmonic coupling which in general allows for large local electrical fields was also studied to enhance the emission of SiV centers in microdisk cavities[9], in the vicinity of gold nanoparticles[10], and in hybrid metal-diamond structures[11].

In this work, we present the integration of SiV centers in nanodiamonds with double bowtie nanoantenna structures, which is shown to cause an enhancement in their photoluminescence (PL) emission. A single nanodiamond is pre-characterized and transferred to the gap of a gold nanoantenna by the "pick and place" technique with the help of a nanomanipulator with a tungsten tip. We show that the PL spectrum of the nanodiamond is modified depending on the geometry of the nanoantenna as well as the position of the emitter in the gap. This provides us with flexibility in designing the nanoantennas to accurately predict and shape the emitters' PL spectrum as desired.

II. Nanodiamond Characterization – Photoluminescence Spectroscopy

A solution of *100 nm* ~~CVD grown~~ nanodiamonds ~~is~~ was spin-coated on a clean ~~i~~Iridium substrate ~~(5 drops of 5 µL each)~~. To ensure that a pre-characterized nanodiamond exhibiting preferred optical properties (eg. narrow linewidth, high count rate) will later be found again, the iridium substrate was engraved with reference cross markers produced by a focused ion beam prior to the spin-coating process. The nanodiamonds were produced by milling a diamond film grown by chemical vapour

We should add a note that both authors contributed equally.
Christoph
03/24/2017 21:19

If we include Christoph Pauly we also have to include his boss: Frank Mücklich. They have a slightly different address: Fachrichtung ...
Christoph
03/24/2017 21:19

Mete did not contribute to this work, so we should not include him here.
Christoph
03/24/2017 21:19

Ref. 6 is on a "Ni" center (although I think this was a SiV as well) – please replace by E. Neu at al., New J. Phys. 13, 025012 (2011). this ...
Christoph
03/24/2017 21:19

True and not true. We have seen 6Mcts/s single photons in nanodiamonds, but also 10.000 cts/s, also in nanodiamonds. Maybe: ...
Christoph
03/24/2017 21:19

Ref: E. Neu et al., Opt. Express 20, 19956 (2012).
Christoph
03/24/2017 21:19

We could add J. Benedikter at al., Phys. Rev. Appl. 7, 024031 (2017).
Christoph
03/24/2017 21:19

I tried to add something to motivate the plasmonic coupling. Please modify if you have better arguments.
Christoph
03/24/2017 21:19

M. Barth et al., J. Lum. **130,** 1628 (2010).
Christoph
03/24/2017 21:19

We don't know the concentration of the NDs in the solution so I don't think it makes much sense to mention the quantity ...
Sarah Lindner
03/24/2017 21:19

deposition. ~~During the diamond growth, sacrificial silicon in the growth chamber caused *in-situ* incorporation of SiV centers in the diamond.~~ After spin-coating, ~~T~~the sample was ~~then~~ placed in ~~the~~ an oven for ~~a couple of~~ 3 hours at *450 °C* to oxidize the surface and remove any residual graphite and amorphous carbon.

In a first step, we identified nanodiamonds which lie is~~t~~olated enough to be picked up and transferred to the antenna structure later on. For that purpose, we recorded high resolution pictures of the sample surface via a commercial confocal laser scanning microscope (Fig.1a)

Next, the samples were tested ~~under~~ using a home-built confocal microscopy setup to identify nanodiamonds hosting SiV centers with the preferred optical properties. ~~where PL scans were performed to identify the presence of SiV centers in the nanodiamonds.~~ In this setup, the sample is either illuminated with diffuse white light to investigate the sample surface, or with ~~The setup includes~~ a red diode laser (Schaefter-Kirchhoff , λ_{ex} = *660 nm*) that is ~~made incident~~focused on the studied sample through a *100X*, *NA = 0.8* microscope objective to study the fluorescence of SiV centers in diamond. The same objective serves to collect light stemming from the sample. The collected light can be guided to a CCD camera, avalanche photo diodes (APDs), or a spectrometer.

To identify the nanodiamonds on the sample surface, the sample is illuminated with diffuse white light and the collected light is guided to a CCD camera. The optical image in Fig. 1b shows a picture of the sample surface under white light illumination. White spots correspond to nanodiamonds that might contain SiV centers. They appear as bright spots due to the scattering caused by the white light illumination. The two bright lines correspond to two cross markers that were previously engraved on the surface of the sample ~~as references for locating specific nanodiamonds later on~~.

~~The emitted signal is collected through the same objective and directed to a silicon CCD camera and a spectrometer.~~

~~The optical image in Fig. 1a shows white spots corresponding to nanodiamonds that might contain SiV centers. They appear as bright spots due to the scattering caused by the white light illumination. The two bright lines correspond to two crosses that were previously engraved on the surface of the sample before the deposition of the solution and serve as references for locating specific nanodiamonds later on.~~

In order to test the presence of SiV centers in the nanodiamonds and to pre-select nanodiamonds hosting SiV centers with desired optical properties, such as narrow linewidth and high countrates, the sample is excited with the red laser and photoluminescence (PL) scans and spectra ~~were~~ are recorded. A long pass filter (*λ = 720 nm*) is placed in the detection path to suppress any signal stemming from the laser.~~performed on the sample where~~. During the PL scan, the laser spot scans the surface and the emitted PL is recorded by the APD. In front of the APD a 730-750nm bandpass filter is installed. The center wavelength of the zero-phonon line of an SiV center is located at around *738 nm*. Therefore, ~~I~~if a nanodiamond contains an SiV center, its emission ~~peak will be located at around *737 nm* which~~ will results in a bright spot in the PL scan. ~~A long pass filter (*λ = 720 nm*) is placed at the entrance of the spectrometer to eliminate any signal coming from the laser.~~ Fig. 1~~c~~b shows an example of a PL scan where bright spots (highlighted by the red circles) correspond to nanodiamonds ~~that act as potential candidates for hosting~~ with PL in the SiV centers spectral range. To further verify the presence of SiV centers, PL spectra at room temperature are recorded. ~~As seen~~

The nanocrystalline diamond starting material was directly grown on a silicon wafer. A microwave hydrogen plasma containing 1% methane was used to grow on purified 5nm nanodiamond seeds (produced by PlasmaChem). To induce in-situ SiV center creation, sacrificial silicon pieces are situated in the growth chamber. The diamond is then milled by a wet-milling process in a vibrational mill with steel beads to crystals of average diameter of 100nm . The particle size was determined with laser diffraction spectroscopy.

I think it would be fair to also include the nanodiamond producers – they often get not included as authors in the papers that use their material… what do you think? If so, we have to add L.Gines and O. Williams, Cardiff University and A. Muzha and A. Krüger, University of Würzburg.

Christoph
03/24/2017 21:19

What are these? Narrow emission linewidth and high PL count rate? Or cancel here because it's mentioned again below: "…identify…hosting SiV centers."
Christoph
03/24/2017 21:19

That's all contained in the paragraph just above…

Christoph
03/24/2017 21:19

Where?

Christoph
03/24/2017 21:19

~~in~~ Fig. 2 shows a representative spectrum~~;~~ where the intense narrow peak (*λ = 738.55 ±0.01nm*, *Δλ = 5.09±0.03 nm*) ~~in the spectrum~~ corresponds well ~~with~~to the zero phonon line (ZPL) of ~~the~~unstrained SiV centers and therefore allows us to deduce that the studied nanodiamond ~~might~~ contains at least one SiV center.

Sure that the spectrometer reaches this resolution? I thought it's more like 50 GHz = 0.1 nm.
Christoph
03/24/2017 21:19

Is this the one nanodiamond that has been used in the following investigations?
Christoph
03/24/2017 21:19

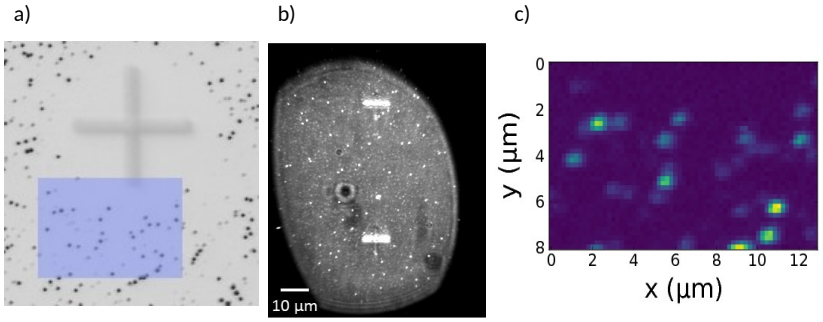

Fig. 1 a) Picture recorded with a commercial high resolution laser scanning microscope. The area shaded in blue represents the PL scan in image 1c. ~~a~~b) ~~Optical i~~Images of the sample surface ~~–~~of 100 nm CVD-grown nanodiamonds spin-coated on an Iridium substrate illuminated with diffuse white light. The white bars are the horizontal bars of the cross markers which serve as a coarse orientation on the sample surface, the white dots are nanodiamonds, the big black spot is an artifact. b) Photoluminescence scan of a ~~*50 × 50*~~ *8x13 µm* area on the sample. ~~Red circles~~Bright dots correspond to nanodiamonds that might contain SiV centers.

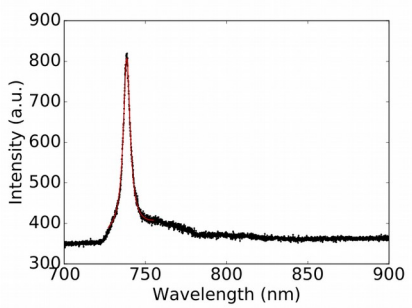

Fig. 2 PL spectrum of a nanodiamond at room temperature. Black: experimental results; red: fit to experimental data, which yields the following values: ZPL center wavelength *λ = 738.55 ±0.01nm*, linewidth *Δλ = 5.09±0.03 nm.*

III. Double Bowtie Nanoantennas - FDTD Numerical Simulations and Fabrication

Maybe add one introductory sentence here why the special form of the double bowtie antenna has been chosen? Is there a reference for the design?
Christoph
03/24/2017 21:19

FDTD numerical simulations were performed using Lumerical software to characterize gold double bowtie nanoantennas on a gold substrate. The nanoantennas have a gap of *g = 150 nm* (taking into account the diameter of the nanodiamonds of around *100 nm*), side length of *L = 2 µm*, and a thickness of *t = 60 nm* (see Fig.3a). Upon excitation with incident light, an intense electromagnetic hotspot is formed in the nanoantenna gap[12], which is expected to excite a nanodiamond containing SIV centers aiming to enhance its fluorescence emission.

Shouldn't we say here (or in a sentence before) that the design was tailored or optimized for incorporating NDs of 100 nm size?
Christoph
03/24/2017 21:19

Unlike a single bowtie that is sensitive only to the polarization along its principle axis (C2 rotational symmetry), a double bowtie features a C4 rotational symmetry and therefore focuses both parallel and perpendicular polarizations. For that, a circularly polarized light with a wavelength range of $\lambda = 400 - 1500\ nm$ is chosen to illuminate a gold double bowtie nanoantenna on a gold substrate, which efficiently excites both the horizontal and vertical components of the structure. The index of refraction of gold is taken from Palik[13], and that of the nanodiamond is chosen to be $n = 2.4$ at $\lambda = 660\ nm$. The electric field intensity in the nanoantenna gap is then measured as a function of wavelength to identify the antenna resonance. The spectrum is given in Fig.3b where we observe that the resonance shows two peaks; an intense peak coinciding with the SiV emission wavelength ($\lambda = 739\ nm$), and an additional mode at a lower wavelength ($\lambda = 710\ nm$). The resonance spectrum of the antenna alone shows only one peak at 739 nm. Thus, the additional peak is attributed to the presence of the nanodiamond that is slightly shifted from the center of the gap, corresponding to our experimental conditions.

I think one has to mention before that we do not only simulate the antenna structure but also directly incorporate the nanodiamond into the simulations.
Christoph
03/24/2017 21:19

Maybe also show the spectrum of the antenna w/o nanodiamond (e.g. as dotted line in Fig 3b)
Christoph
03/24/2017 21:19

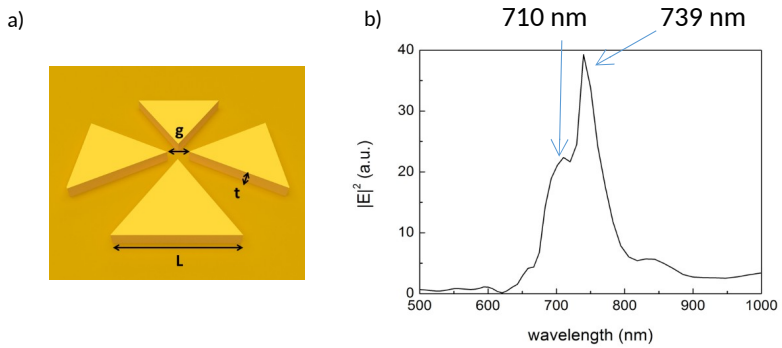

Fig.3. a) Schematic of a double bowtie nanoantenna with side length L, thickness t and gap g, b) Electric field intensity as a function of wavelength measured in the gap of a double bowtie nanoantenna containing a nanodiamond

The structures were ~~then~~ fabricated by electron beam lithography (EBL). A 200 nm layer of polymethyl methyl acrylate (PMMA) is first deposited on a clean silicon substrate. This is followed by e-beam exposure to engrave the desired design on the substrate, after which a 60 nm layer of gold is evaporated to cover both the antennas and the substrate underneath. An SEM image of the fabricated gold double bowtie nanoantennas is shown in Fig.4.

Just to get this right: PMMA is used as a mask, exposed by e-beam, but then the pattern needs to be transferred to the substrate, thus I guess there must be an etching step?
Christoph
03/24/2017 21:19

Have there only been fabricated antennas with 150nm gap and 2 micron length or with different parameters?
Christoph
03/24/2017 21:19

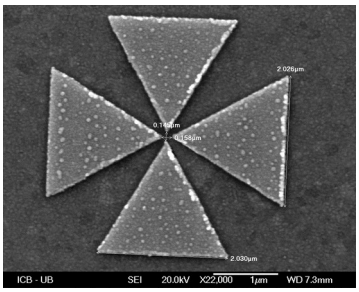

Fig.4. SEM image of a gold double bowtie nanoantenna on a gold substrate with gap size g=150 nm and side length L=2μm

IV. Nanodiamond Manipulation – Pick and Place technique

After the a nanodiamond was pre-selected according to ~~desired optical properties as described in section II on the substrate engraved with cross markers,~~the procedure outlined in Sec. II, ~~N~~nanodiamond manipulation ~~was performed by~~we used the "pick and place" technique~~, which allows us~~ to transfer nanodiamonds, with the help of a nanomanipulator ~~s, a nanodiamond that was oxidized (heated at 450 °C) and well-prepared on a separate substrate .(i.e. with good optical properties)~~ to the sample containing the nanoantenna structures (schematic in Fig. 5). A nanomanipulator with a tungsten tip (radius of curvature = *100 nm*, sharpened by a focused ion beam) is incorporated inside an SEM, which allows us to visualize and manipulate the nanodiamonds at the same time. The two samples~~,~~ i.e. ~~*100 nm*~~ nanodiamonds on ~~Iridium~~ the substrate~~,~~ and the gold nanoantenna samples, are placed inside the SEM. The tip is approached to the surface and gets in contact with the desired pre-characterized nanodiamond registered to the markers on the substrate. This procedure was ~~done~~ performed ~~on~~ for the nanodiamond ~~that was~~ characterized in section 2~~, and corresponding to the intrinsic~~ (with PL spectrum as given in Fig.2). ~~Counting on the~~Due to Van der Waals forces between the tip and the nanodiamond, the latter successfully sticks to the tip, as seen in Fig. 6a. The tip is then moved to the second sample and carefully approached to the gap of the target nanoantenna. When the nanodiamond touches the surface, and also due to the existing Van der Waals forces, it gets off the tip and lies precisely in the gap, as demonstrated in Fig. 6b (the nanodiamond is the black dot in the gap).

"the" or "a"?

Christoph
03/24/2017 21:19

Maybe it's better to write 'adhesion', I'm not sure if it's really van der Waals forces

Sarah Lindner
03/24/2017 21:19

... adhesion forces between nanodiamond ans surface result in separation from the tip and precise placement in the antenna gap, as demonstrated...

Christoph
03/24/2017 21:19

See above

Sarah Lindner
03/24/2017 21:19

It's blue-green colored now...

Christoph
03/24/2017 21:19

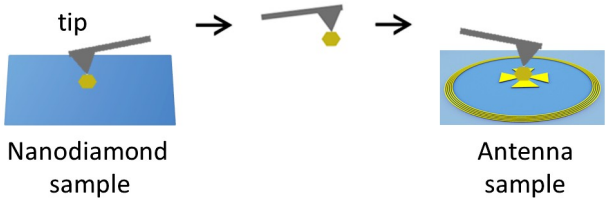

Fig.5. Schematic of the pick and place technique.

a) b)

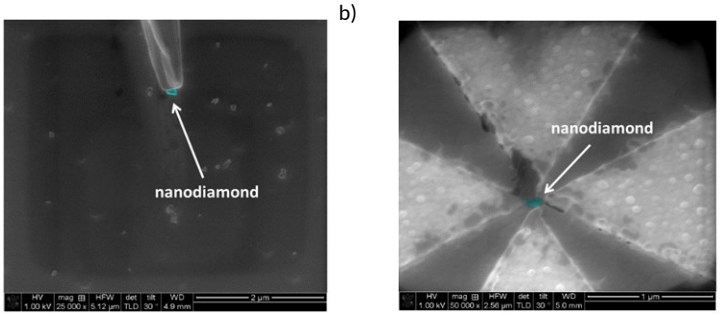

Fig.6. Pick and Place technique for nanodiamond manipulation, nanodiamond colored blue in the image; a) nanodiamond stuck to the tip and was lifted off the substrate b) nanodiamond layed off in the nanoantenna gap.

~~Consequently~~After this deterministic placement,~~—~~ we measure the PL spectrum of the nanodiamond ~~is measured~~ to identify the effect of the nanoantenna on its emission. The result is ~~given~~ displayed in Fig. 7a where an increase in the PL intensity is observed by more than a factor 10 ~~(was the laser intensity roughly the same one in order to obtain Fig 2 and Fig 7-a?)~~ indicating that the nanoantennas indeed contribute ~~in~~ to the enhancement of the SiV centers emission. A $\lambda = 710\ nm$ long pass filter is used to eliminate any signal from the laser. The additional peak at a lower wavelength is attributed to the antenna resonance mode. To verify this, we convolute the experimental PL spectrum of the nanodiamond measured before placing it in the nanoantenna (Fig. 2) with the intensity spectrum of the nanoantenna obtained by simulations (Fig. 3b). The result~~ing~~ spectrum is given in Fig. 7b, ~~which~~ and ~~shows identical peaks as the ones~~ is in good agreement with the ~~peak~~measured spectrum in Fig. 7a, confirming that indeed the extra peak is due to the antenna resonance.

a) 726 nm 739 nm b) 727 nm 739 nm

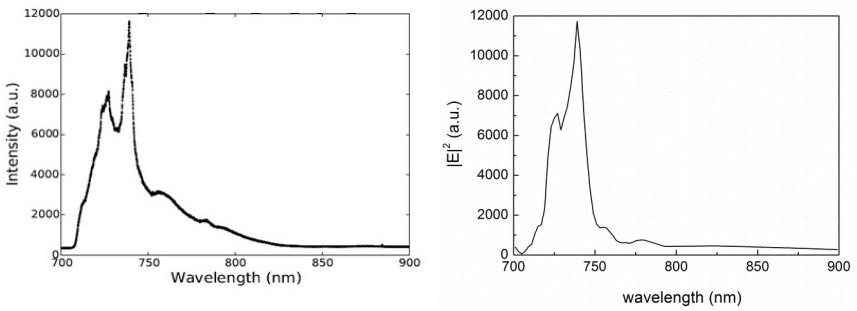

Fig.7. a) Experimental PL spectrum of the nanodiamond after placing it in the nanoantenna, b) Convoluted spectrum of the experimental PL spectrum of the nanodiamond (see Fig. 2) with the simulated resonance spectrum of the nanoantenna (see Fig. 3b)

V. Conclusion

I like that viewgraph!!

Christoph
03/24/2017 21:19

We have to state whether the excitation conditions were the same or at least comparable and that the integration times for Figs. 2 and 7 were the same (were they?).
The enhanced emission might have two origins: (i) Purcell factor shortening the SiV lifetime giving rise to larger emission per time interval; (ii) rotation of the nanodiamond upon pick and place resulting in a varied dipole orientation which results in a larger collection efficiency; (iii) modified radiation pattern from the antenna as compared to the dipole pattern which leads to a larger collection efficiency.
Have you calculated the latter effect?? I guess this one is important. (ii) could have been measured by looking at the polarization direction of the emitted light.

Christoph
03/24/2017 21:26

Yes. However, it's neither a single color center nor do we know the dipole orientation

Sarah Lindner
03/24/2017 21:19

Correct?

Christoph
03/24/2017 21:19

In this work, we presented the successful integration of single photon sources, namely SiV centers in nanodiamonds, to plasmonic nanoantenna structures. This was done achieved by the "pick and place" technique which was usedallowing to transfer a single nanodiamond with SiV centers to the gap of a double bowtie nanoantenna. Optical characterization, sample fabrication, as well as numerical FDTD simulations were performed to study our plasmonic structures. Photoluminescence measurements showed a significant increase in the emission intensity of the nanodiamond after placing it in the nanoantenna gap. We conclude that careful optimization of various parameters such as the geometry of the antenna, the materials used, and the position of the emitter in the gap, provides flexibility in defining the resulting PL spectrum of the nanodiamond, which can be adjusted according to the desired application.

The shown data stems from multiple SiVs

Sarah Lindner
03/24/2017 21:19

Further work including lifetime measurements is necessary to give an accurate description of the emission enhancement of the nanodiamond. In addition, the success of our manipulation technique encourages us to go further with this experiment and apply it to nanodiamonds containing only one single SiV center. This includes saturation and second order correlation measurements to probe single SiV centers, and consequently quantify the exact Purcell enhancement imposed by the nanoantenna on a single photon emitter.

References

1. Rittweger, E., Han, K. Y., Irvine, S. E., Eggeling, C. & Hell, S. W. STED microscopy reveals crystal colour centres with nanometric resolution. *Nat. Photonics* **3,** 144–147 (2009).
2. Maurer, P. C. *et al.* Far-field optical imaging and manipulation of individual spins with nanoscale resolution. *Nat. Phys.* **6,** 912–918 (2010).
3. Togan, E. *et al.* Quantum entanglement between an optical photon and a solid-state spin qubit. *Nature* **466,** 730–734 (2010).
4. Dutt, M. V. G. *et al.* Quantum Register Based on Individual Electronic and Nuclear Spin Qubits in Diamond. *Science* **316,** 1312–1316 (2007).
5. Aharonovich, I. *et al.* Diamond-based single-photon emitters. *Rep. Prog. Phys.* **74,** 76501 (2011).
6. Siyushev, P. *et al.* Low-temperature optical characterization of a near-infrared single-photon emitter in nanodiamonds. *New J. Phys.* **11,** 113029 (2009).
7. Muller, T. *et al.* Optical signatures of silicon-vacancy spins in diamond. *Nat. Commun.* **5,** (2014).
8. Riedrich-Moller, J. *et al.* Deterministic Coupling of a Single Silicon-Vacancy Color Center to a Photonic Crystal Cavity in Diamond. *Nano Lett.* **14,** 5281–5287 (2014).
9. Lee, J. C., Aharonovich, I., Magyar, A. P., Rol, F. & Hu, E. L. Coupling of silicon-vacancy centers to a single crystal diamond cavity. *Opt. Express* **20,** 8891 (2012).
10. Orlanducci, S., Cianchetta, I., Tamburri, E., Guglielmotti, V. & Terranova, M. L. Effects of Au nanoparticles on photoluminescence emission from Si-vacancy in diamond. *Chem. Phys. Lett.* **549,** 51–57 (2012).
11. Song, J. *et al.* Plasmon-enhanced photoluminescence of Si-V centers in diamond from a nanoassembled metal-diamond hybrid structure. *CrystEngComm* **16,** 8356 (2014).
12. Rahbany, N. *et al.* Integrated plasmonic double bowtie / ring grating structure for enhanced electric field confinement. *Nanospectroscopy* **1,** (2015).
13. Palik, E. D. *Handbook of optical constants of solids*. **3,** (Academic press, 1998).