Enhancing fluorescence of diamond vacancy centers near gold nanorods via geometry optimization

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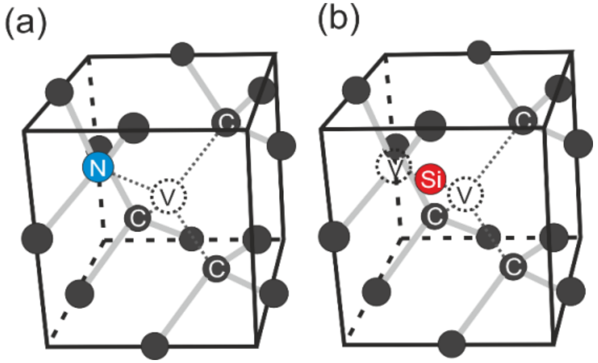
Importance of fluorescence enhancement and role of nanoparticles in realization

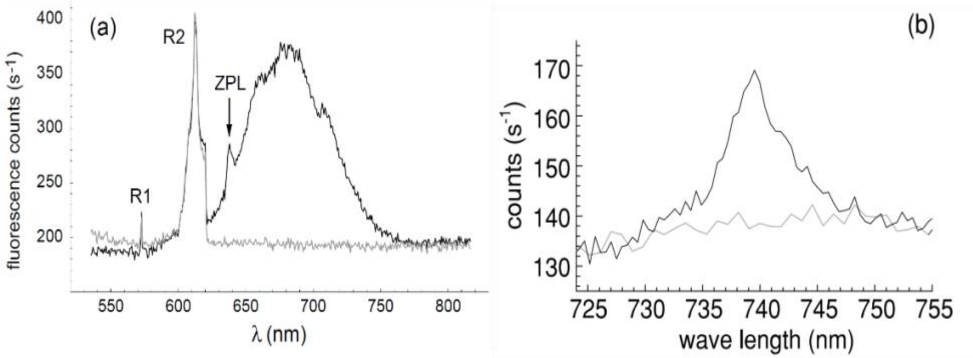
Detection of light in fundamental research and in applications (QIP, solid-state physics, analitical chemistry and medicine)

Improve detection=>Fluorescence enhancement => enhancement of excitation and emission rate of molecules

One possible way: Enhancement via metal nanoparticles (gold and silver nanoparticles, e.g. nanorods)

Potential single-photon sources:
nitrogen (NV) and silicon (SiV) diamond color vacancy centers





NV excitation: 532 nm
NV emission: 650 nm

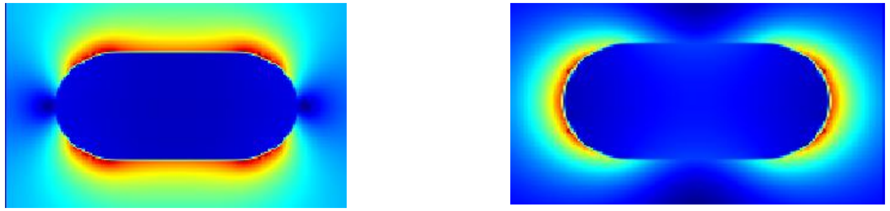
SiV excitation: 532 nm
SiV emission: 738 nm,
perpendicular orientation of dipoles corresponding to excitation and emission

M. Pelton et al.: *Phys. Rev. Lett*. **89**, (2002): 233602
S. Lal et al.: *Nat. Photonics* **1**, (2007): 641–648
C. Zander, J. Enderlein, R.A. Keller: VCH-Wiley: Berlin, (2002)
H. G. Craighead, *Nature* 442, (2006): 387–393
C. Want et al.: *J. Phys. B* **39** (2006): 37
L. J. Rogers et al.: *Phys. Rev. B* **89** (2014): 235101.

Approach for diamond color centers' fluorescence enhancement via metal nanoparticles

Physical background

1. Localized surface plasmon resonance



- Exciting light couples into electron plasma oscillation (plasmon)
- Confine **E**-field
- Increases local field density (LDOS)

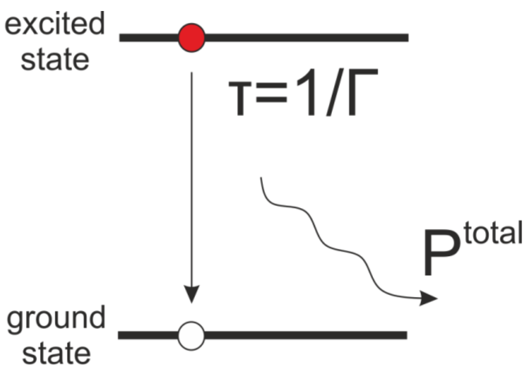
-> excitation rate enhancement

$$\gamma^{excitation} / \gamma_0^{excitation} = \left|\vec{p}\cdot\vec{E}\right| / \left|\vec{p}_0\cdot\vec{E}_0\right|$$

reciprocity theorem

$$\left.\frac{\gamma^{radiative}}{\gamma_0^{radiative}}\right|_{emission} = \left.\frac{QE}{QE_0}\right|_{emission} \cdot \left.\frac{\gamma^{radiative}}{\gamma_0^{radiative}}\right|_{excitation}$$

2. Purcell effect

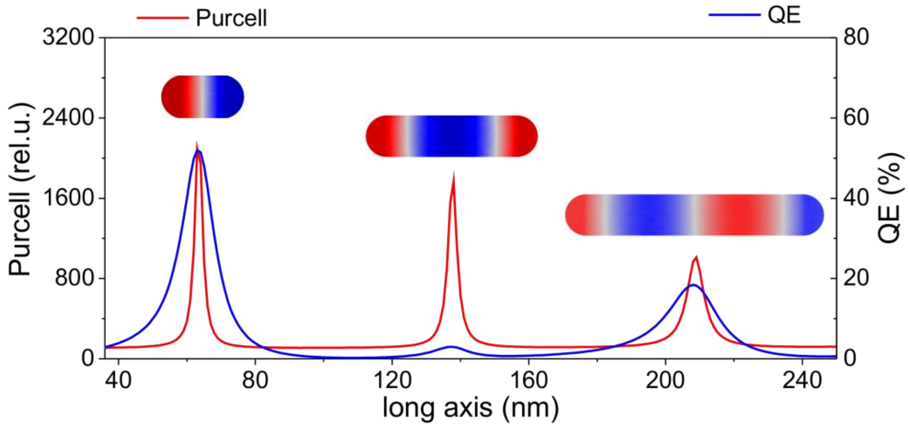


- τ modifies in inhomogeneous environment
- relative enhancement is described by:

$$Purcell = \frac{P^{total}}{P_0^{total}} = \frac{P^{radiative} + P^{non-radiative}}{P_0^{radiative}}$$

Excitation enhancement can be described with Purcell!

3. Antenna effect



- emitted light resonant couples into plasmon of different kinds
- Resonance effects depend on geometry, shape, material

$$QE = \frac{P^{radiative}}{P^{total}}$$

T. H. Taminiau et al.: *Nano Lett.* **7**, (2007): 28–33
E. M. Purcell: *Phys. Rev*. **69**, (1946): 681-681
P. C. Das, A. Puri: *Phys.Rev. B* **65**, (2002): 155416

Approach for diamond color centers' fluorescence enhancement via metal nanoparticles

In conclusion:
resonant frequency tuning via geometry (and material)

Designing nanorods capable of enhancing fluorenscence at "arbitrary" wavelengths

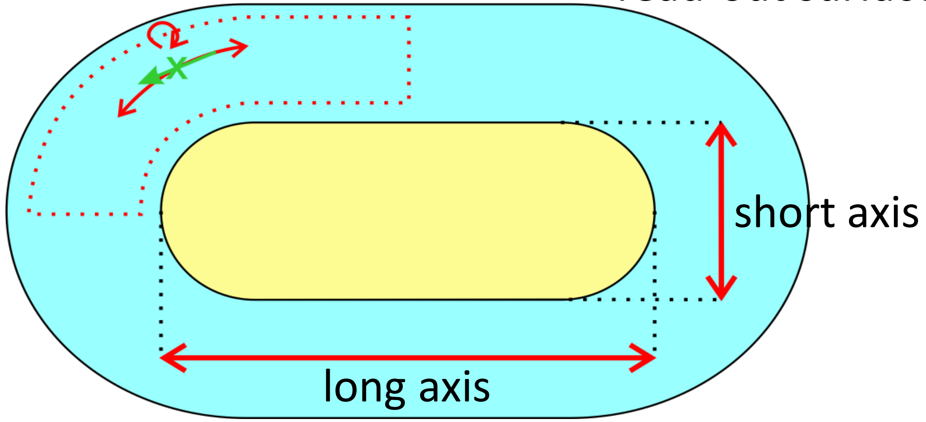
Geometry optimization via COMSOL

External in-house made optimization algorithm:

GLOBAL

- electric point dipole
- materials
- read-out surfaces

dipole position
dipole orientation



Single λ

Radiative rate enhancement = Purcell*QE
(possible objective function)

Trade-off between Purcell and QE

Conditional optimization

Purcell condition OR? QE condition

Dual λ

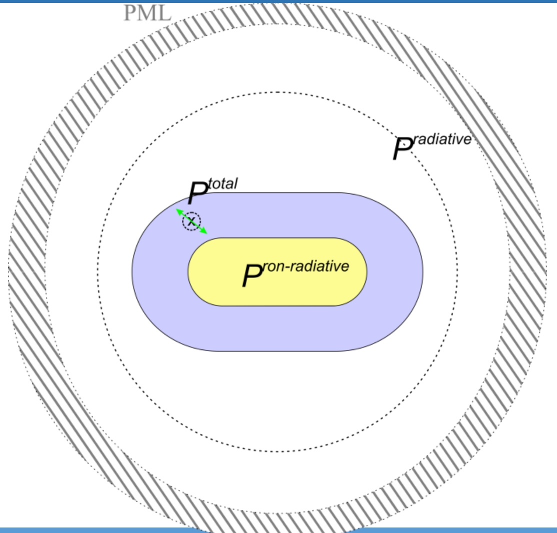
Radiative rate enhancement = $(\text{Purcell*QE})^2$
(possible objective function)

Trade-off between Purcell and QE

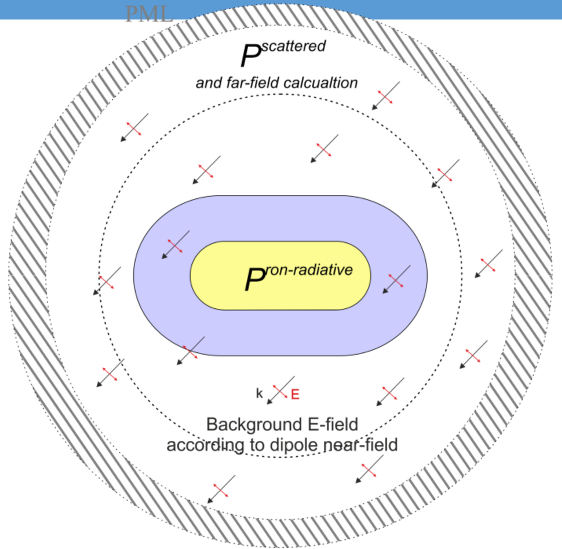
Conditional optimization

Purcell_excitataion & Purcell_emission conditions OR? QE_excitation & QE emission conditions

Modelling and comparative study on scattering cross-section extracted from the near-and far-field



Schematic drawing about the emanating power extraction in the near- and far-field

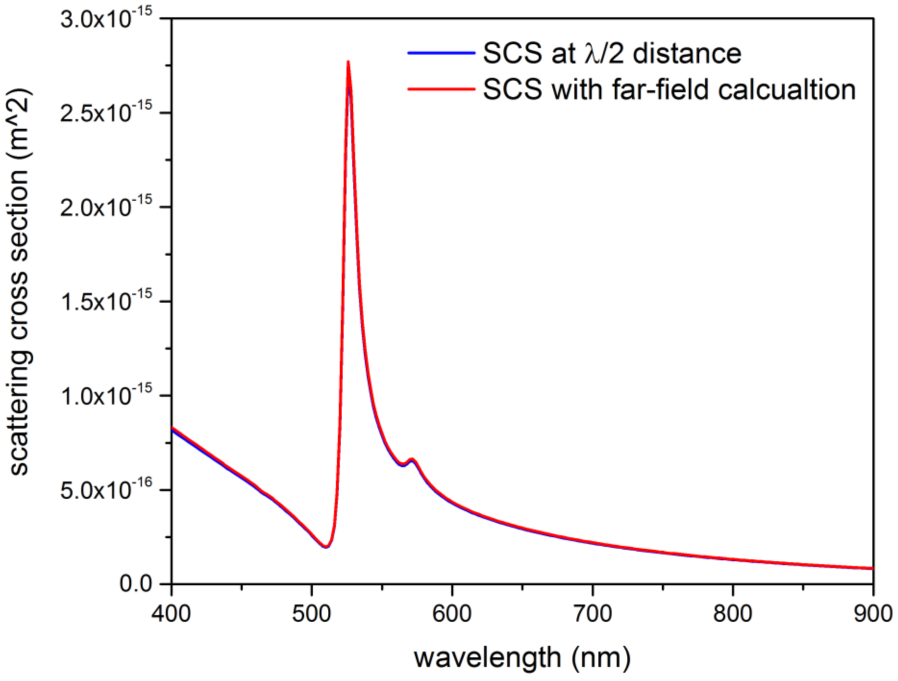


1. Perform the optimization
2. Choose one partial optimum
3. Sweeping wavelength of source
4. Reveal optical response and physics

- Dipole near-field illumination
- Closed surfaces around:
  - dipole to read-out total power
  - structure to read-out radiative power
- Non-radiative power calculated via resistive heating
- PML closes the simulation region
- 3D model is axially symmetric

Is it possible to predict optimal configuration with PW?

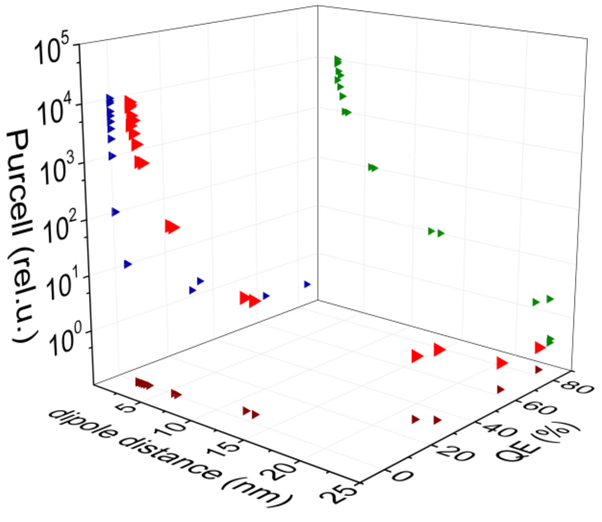
- Linearly polarized plane wave illumination
- Closed surfaces around rod to read-out radiative power
- Far-field calculation
- Non-radiative power calculated via resistive heating



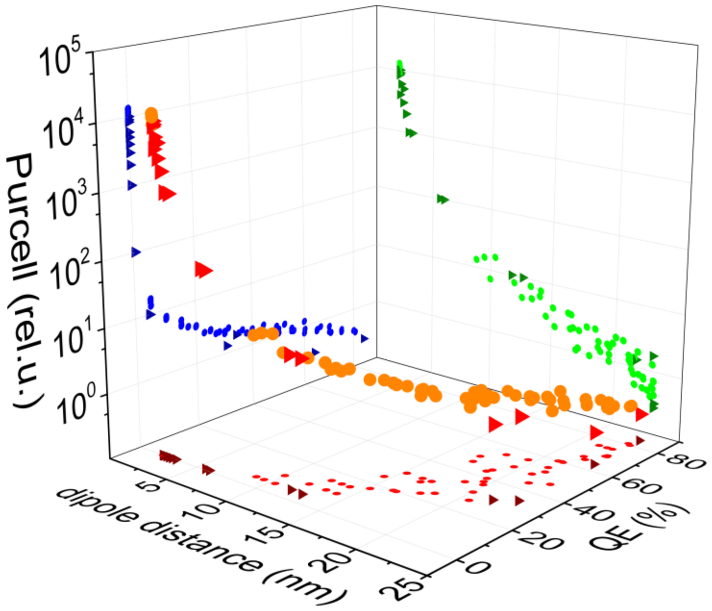
No significant difference between near- and far-field SCS

Purcell~ECS
QE*Purcell~SCS

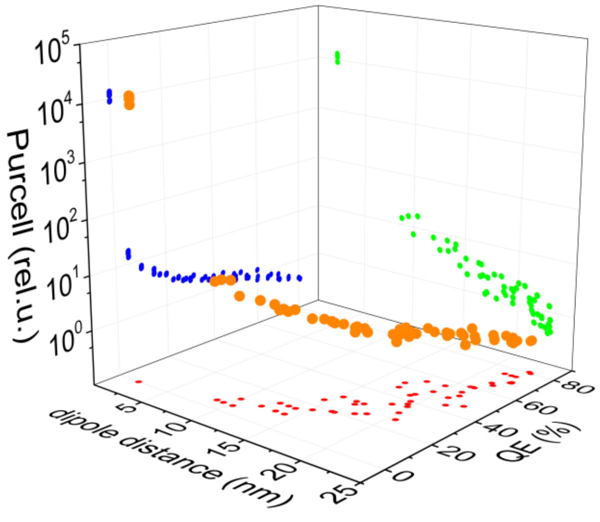
Excitation enhancement of NV and SiV color centers with gold nanorod (532 nm)



QE maximization with Purcell criterion

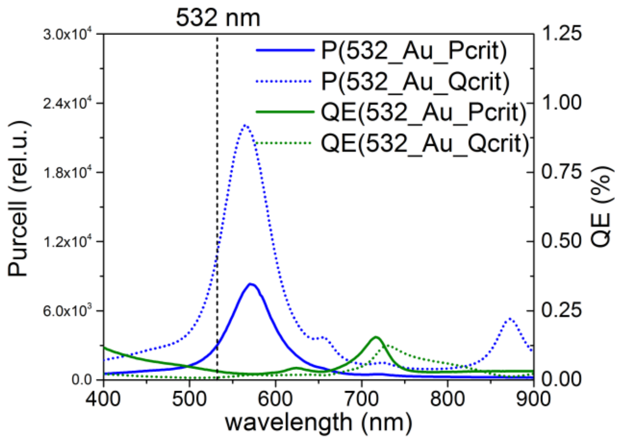


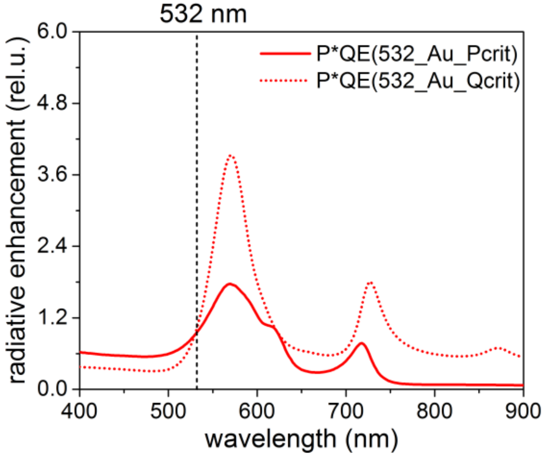
Integrated 3D parameter curve



Purcell maximization with QE criterion

<u>wavelength dependence of optical responses in selected configurations:</u>





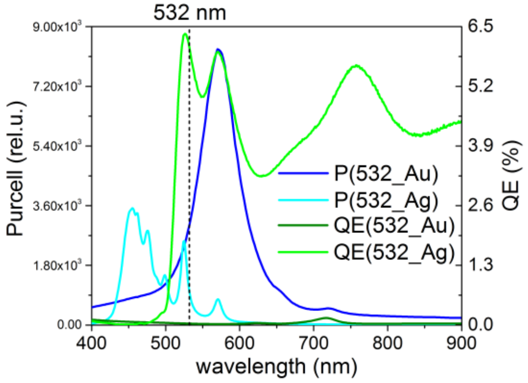
- optimized configurations on the same curve, but in significantly different regions
- Pcrit shows more configurations in large Purcell region
- Qcrit makes it possible to operate with large QE

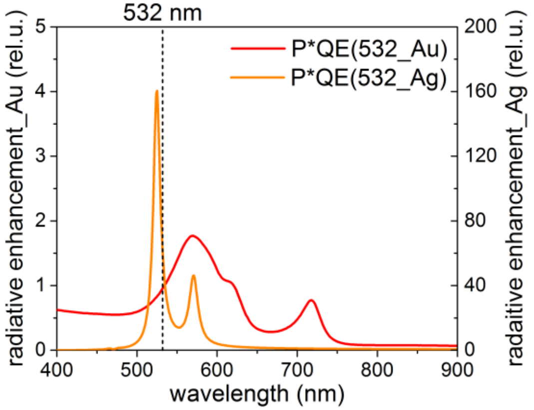
Optical response and cross-sections of selected gold and silver nanorod configurations at NV and SiV excitation wavelength (532 nm)

532	Purcell (rel.u.)	QE (%)	Purcell·QE (a.u.)	long axis (nm)	short axis (nm)	aspect ratio	dipole distance (nm)	inclination (°)
Au	3006.18	0.03	0.96	68.44	15.54	4.4	2.34	74.09
Ag	1076.43	6.06	65.21	22.24	19.37	1.15	4.16	7.97
Ag/Au	0.36	190.25	68.12	0.32	1.25	0.26	1.78	0.11

Considerable excitation enhancement achievable via silver nanorod

Optical response



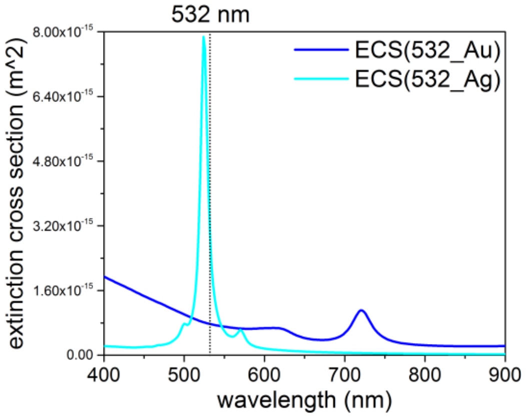


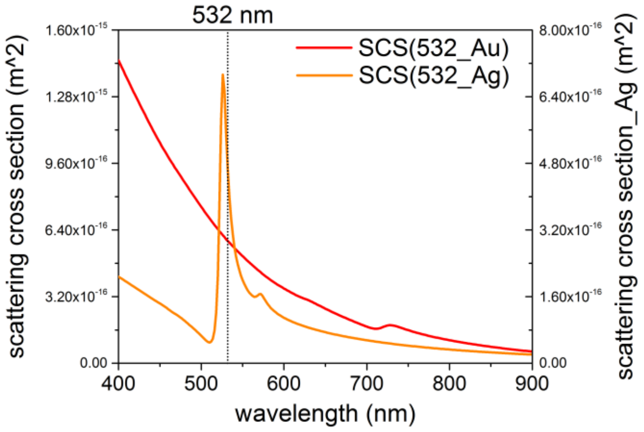
scattering different tendency, coincident Lmax: $\lambda \sim 720$ nm

extinction Lmax ~ Purcell Lmax: same $\lambda \sim 720$ nm

Au

Scattering cross-sections





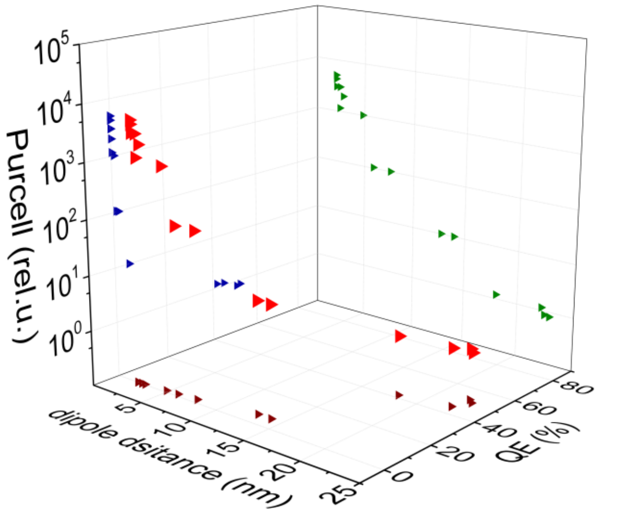
scattering Gmax ~ Purcell*QE Gmax, same $\lambda \sim 532$ nm

extinction Gmax ~ Purcell Lmax, same $\lambda \sim 532$ nm

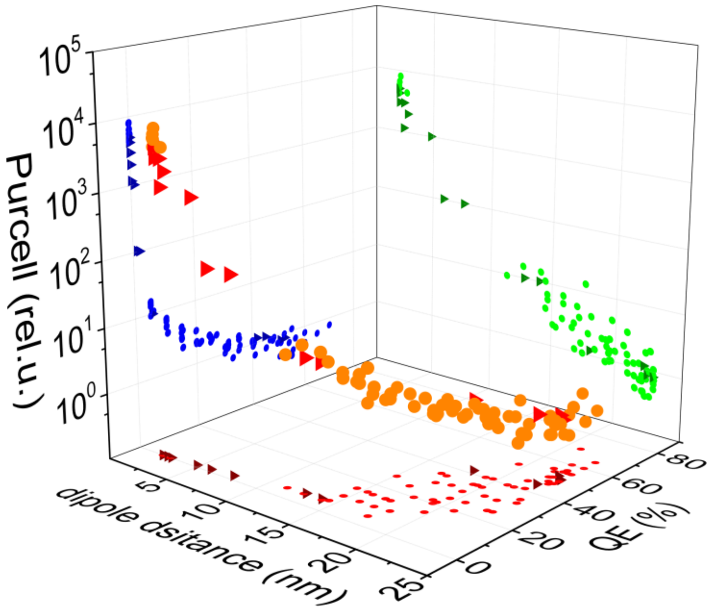
Ag

Coincident peaks in optical response and scattering cross-section at 532 nm only in case of silver

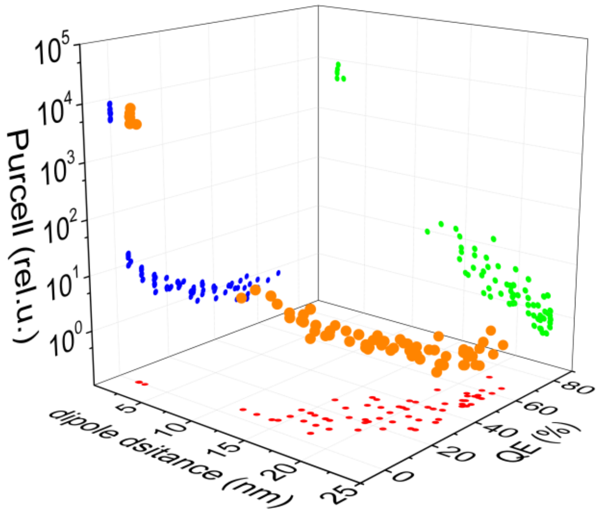
Emission enhancement of NV color centers with gold nanorod (650 nm)



QE maximization with Purcell criterion

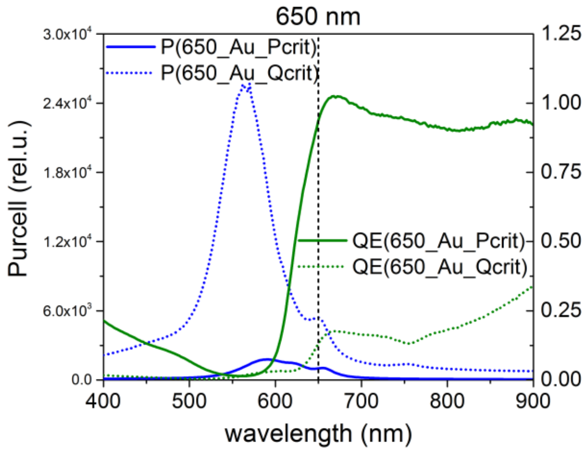


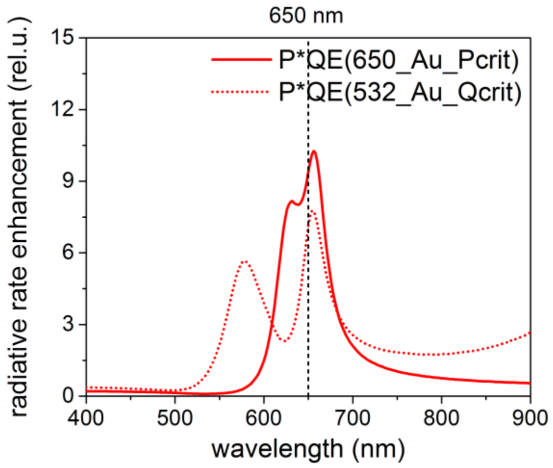
Integrated 3D parameter curve



Purcell maximization with QE criterion

<u>wavelength dependence of optical responses in selected configurations:</u>





- same characteristics of d and QE dependence
- large gap in Purcell vs QE in Qcrit, which makes Pcrit a reasonable choice

<- local maximum of Purcells near 650 nm

<- global maxima of radiative enhancement and QE near and exactly at 650 nm

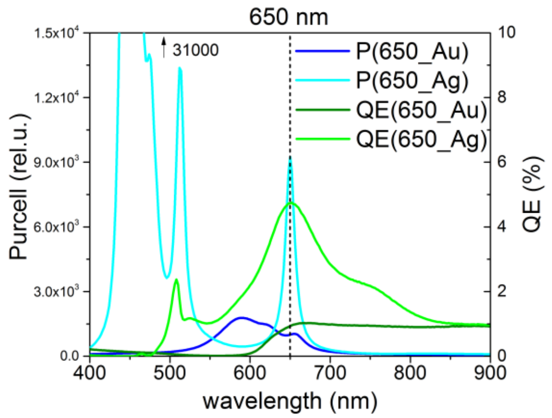
<- multiple maxima appear

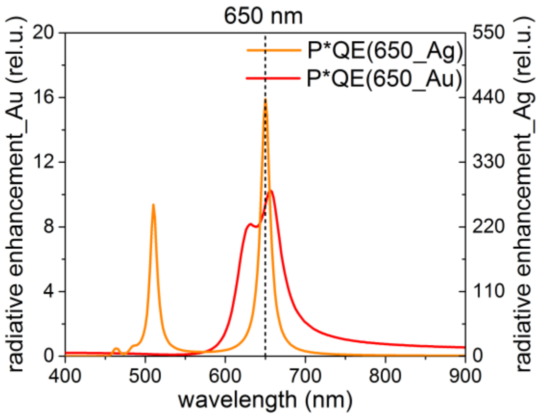
Optical response and cross-sections of selected gold and silver nanorod configurations at NV emission wavelength (650 nm)

650	Purcell (rel.u.)	QE (%)	Purcell·QE (a.u.)	long axis (nm)	short axis (nm)	aspect ratio	dipole distance (nm)	inclination (°)
Au	1002.01	0.94	9.42	20	17.81	1.12	4.78	-8.36
Ag	9262.95	4.73	438.16	24.28	16.51	1.47	2.18	18.91
Ag/Au	9.24	5.03	46.5	1.21	0.93	1.31	0.46	2.26

Considerable emission enhancement achievable via both nanorods, silver is better

Optical response



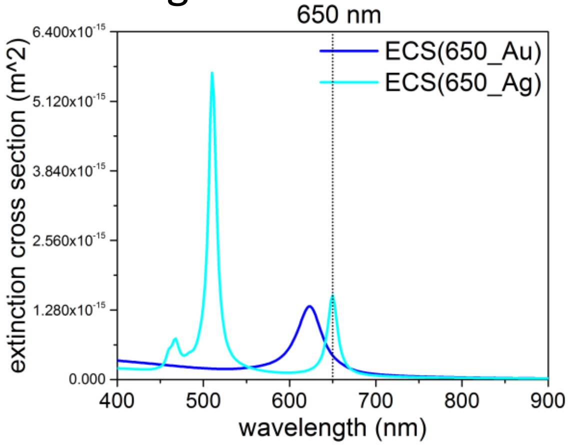


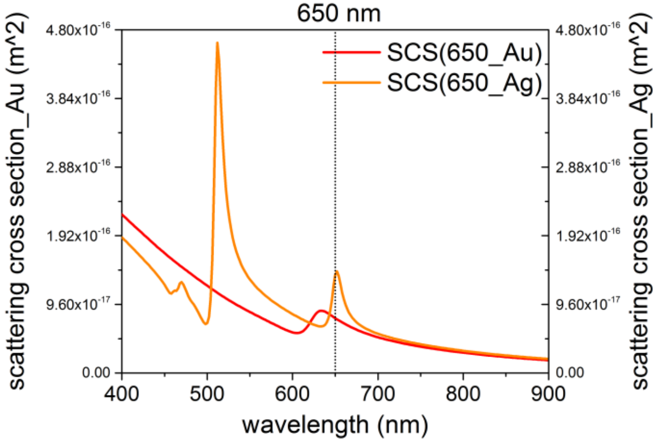
scattering Lmax ~ Purcell*QE Gmax, same λ~650 nm

extinction Lmax ~ Purcell Lmax same λ~650 nm

Au

Scattering cross-sections





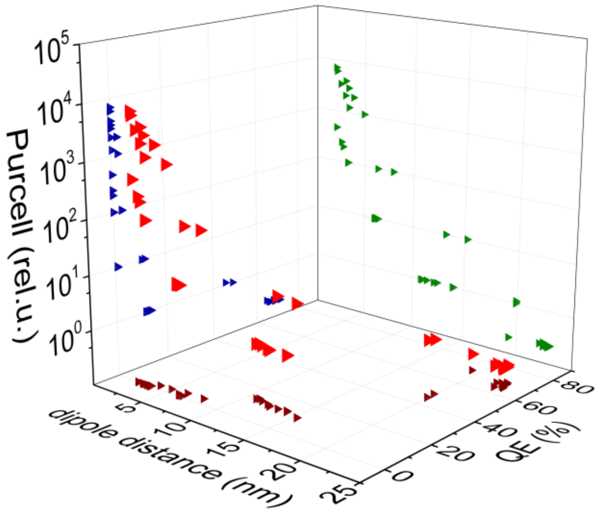
scattering Lmax ~ Purcell*QE Gmax, same λ=650 nm

extinction Lmax ~ Purcell Lmax, same λ=650 nm

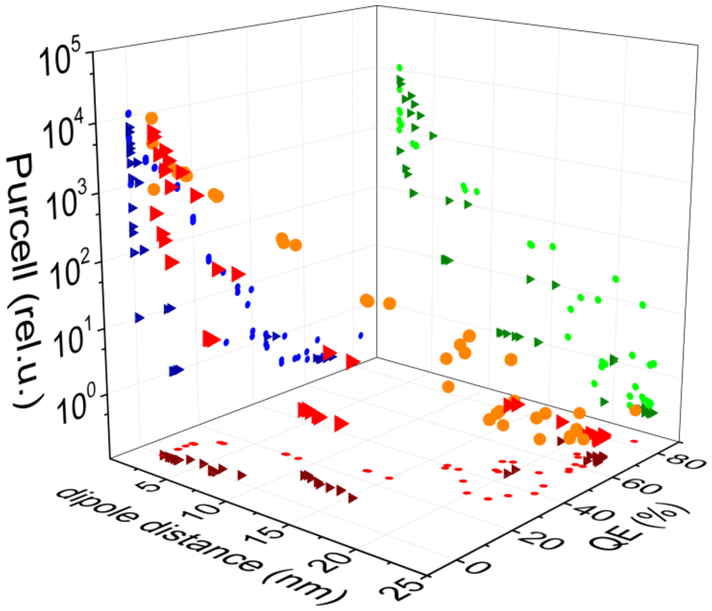
Ag

Coincident peaks in optical response and scattering cross-section at 650 nm in case of both nanorods

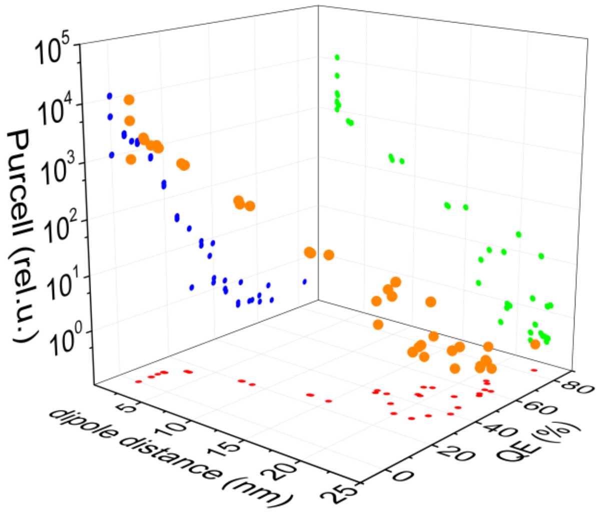
Emission enhancement of SiV color centers with gold nanorod (738 nm)



QE maximization with Purcell criterion

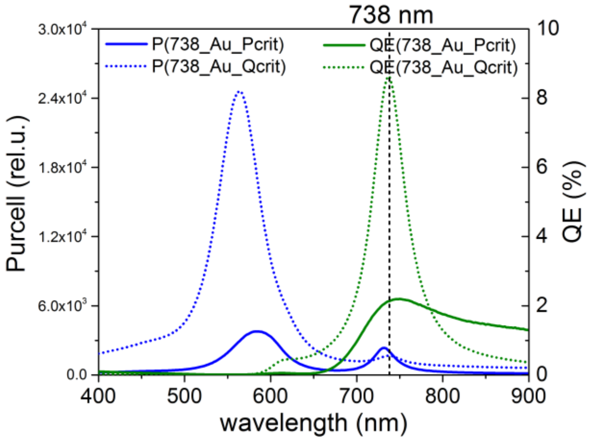


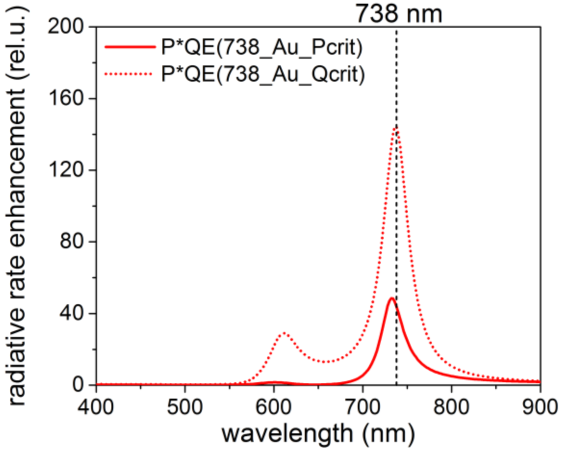
Integrated 3D parameter curve



Purcell maximization with QE criterion

<u>wavelength dependence of optical responses in selected configurations:</u>





- relatively wide distribution is resulted via both optimization methodology
- more configurations with large Purcell vs QE

according to wavelength dependent material properties

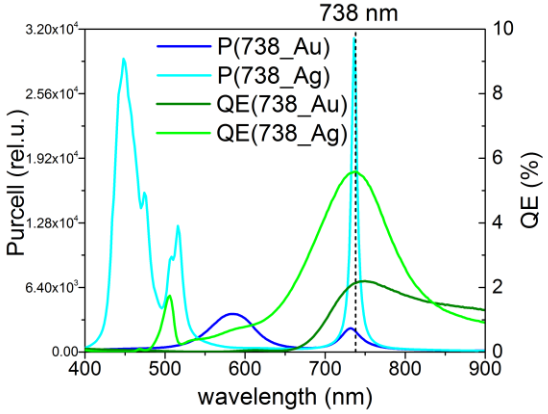
<- local maximum of Purcells close to 738 nm
<- global maxima of radiative enhancement and QE also near or exactly at 738 nm.
<- multiple maxima appear, much larger Purcell at smaller wavelengths

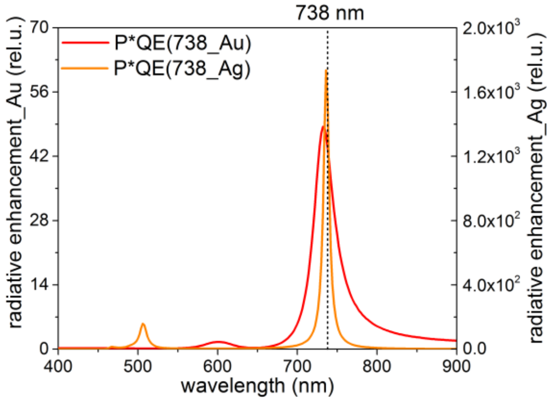
Optical response and cross-section of selected gold and silver nanorod configurations at SiV emission wavelength (738 nm)

738	Purcell (rel.u.)	QE (%)	Purcell·QE (a.u.)	long axis (nm)	short axis (nm)	aspect ratio	dipole distance (nm)	inclination (°)
Au	2050.33	2.15	44.14	28.45	19.56	1.45	3.8	-23.39
Ag	27720.49	5.58	1548.08	25.05	13.73	1.82	2	48.1
Ag/Au	13.52	2.59	35.07	0.88	0.7	1.25	0.53	2.06

Considerable emission enhancement achievable via both nanorods, silver is better

Optical response



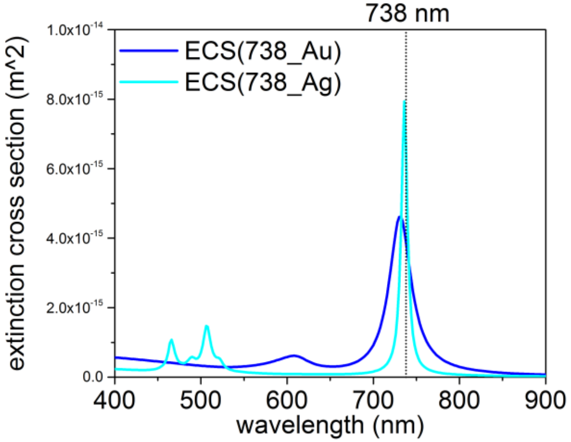


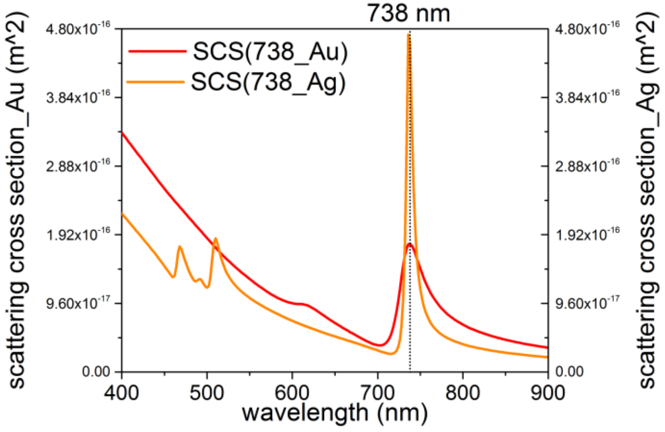
scattering Lmax ~ Purcell*QE Gmax, same λ=738 nm

extinction L/Gmax ~ Purcell G/Lmax, same λ</=738 nm

Au

Scattering cross-sections



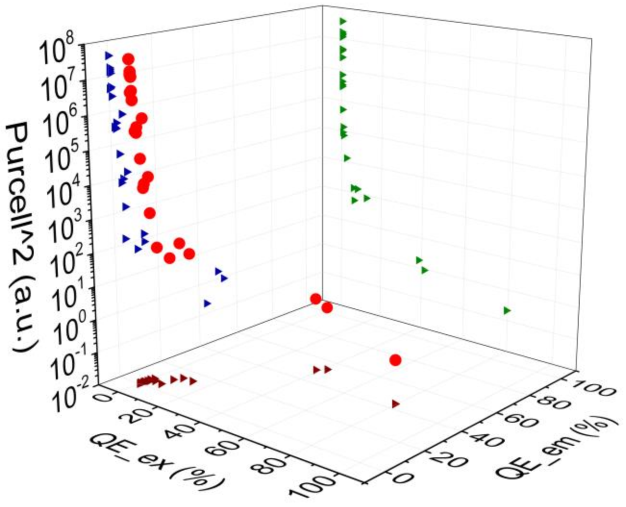


scattering Gmax ~ Purcell*QE Gmax, same λ~738 nm

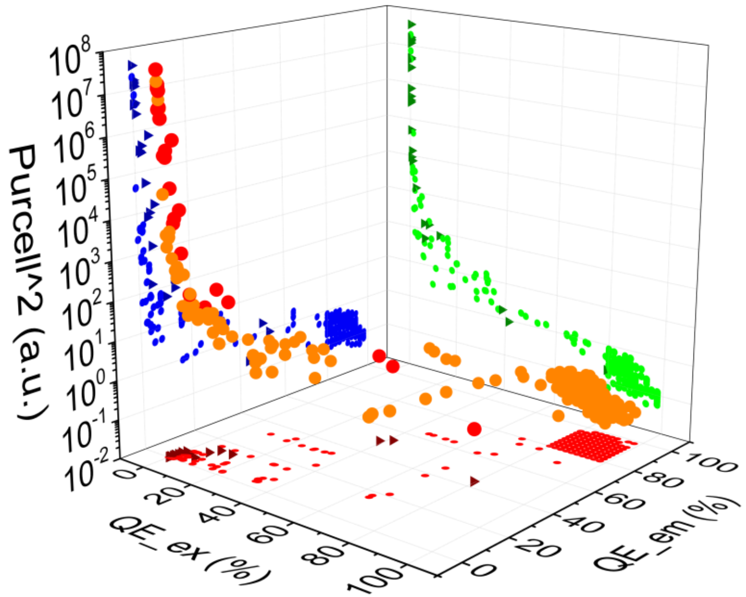
extinction Gmax ~ Purcell Gmax, same λ~738 nm

Ag

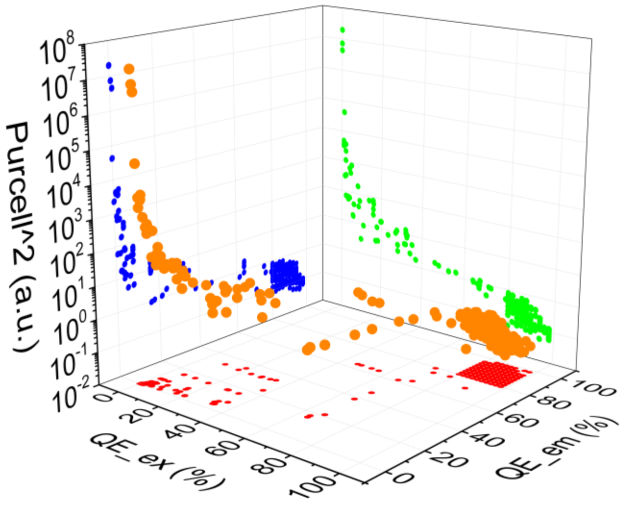
Fluorescence enhancement of NV color centers with gold nanorod (532-650 nm)



QE maximization with Purcell criterion

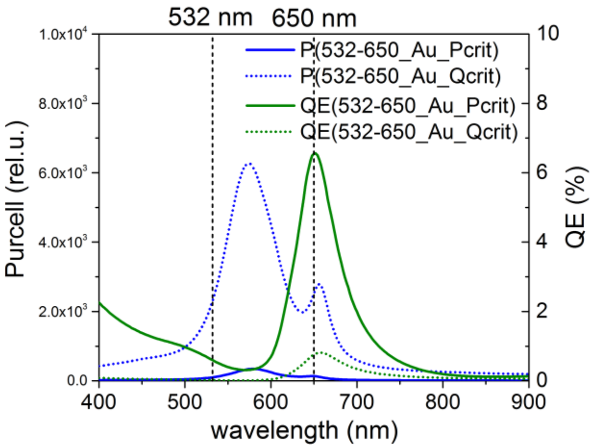


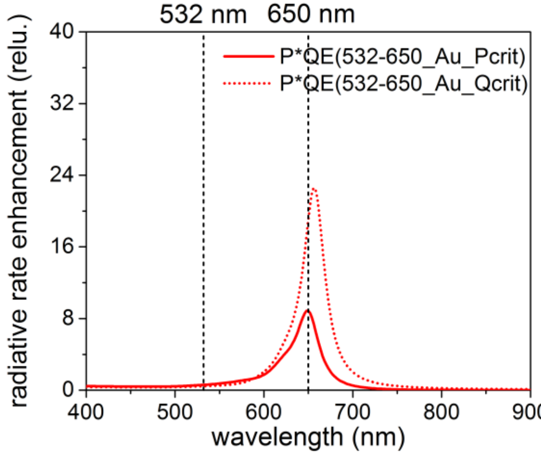
Integrated 3D parameter curve



Purcell maximization with QE criterion

<u>wavelength dependence of optical responses in selected configurations:</u>





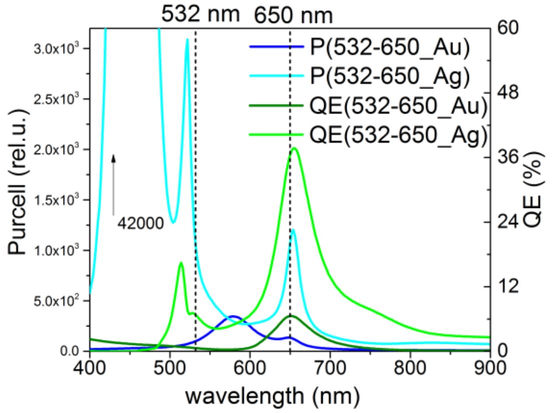
- gaps in both optimization methodologies
- Pcrit still supports large Purcell and small QE
- Qcrit more points in QE [80,100] interval: local search

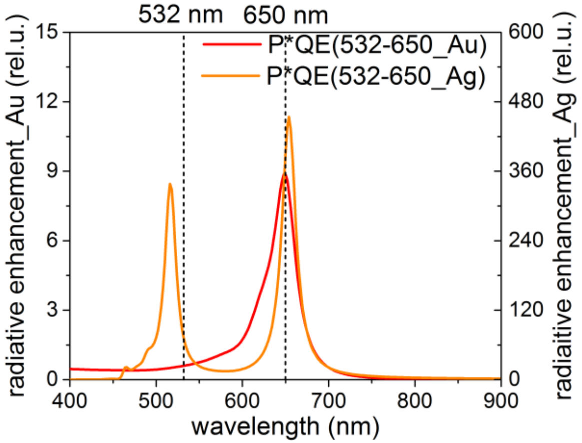
<- local Purcell and global QE & P*QE maxima at 650
gold nanorod does not results in enhancement at 532
(diamond coating shifts resonance peaks)

Optical response and cross section of selected gold and silver nanorod configuration at NV emission and excitation wavelength (532-650 nm)

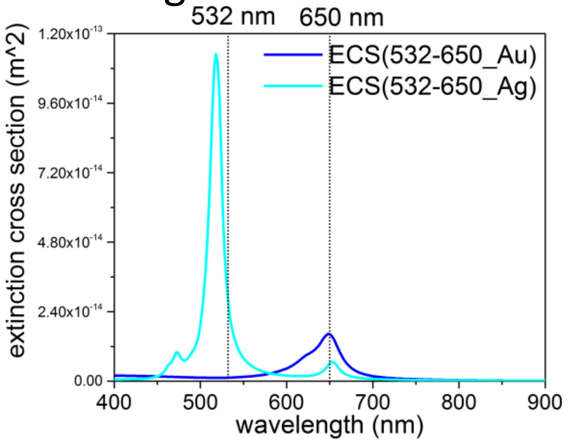
532-650	Purcell (rel.u.) excitation	QE (%) excitation	Purcell·QE (a.u.) excitation	Purcell (rel.u.) emission	QE (%) emission	Purcell·QE (a.u.) emission	(Purcell·QE)^2	long axis (nm)	short axis (nm)	aspect ratio	dipole distance (nm)	inclination (°)
Au	100.35	0.6	0.6	134.77	6.62	8.92	5.37	41.09	37.23	1.1	6.58	24.57
Ag	1005.55	7.2	72.42	915.31	38.65	353.79	25622.65	55.78	37.39	1.49	2.33	-1.61
Ag/Au	10.02	12	120.28	6.79	5.84	39.67	4771.91	1.36	1	1.35	0.35	0.07

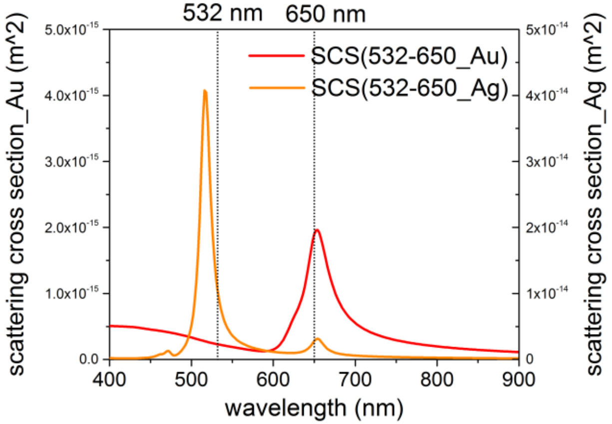
Optical response





Scattering cross-sections





Considerable emission enhancement achievable via both nanorods, silver is better, and results in excitation enhancement as well.

Au

scattering Gmax ~ Purcell*QE Gmax, same λ~650 nm

extinction Gmax ~ Purcell Lmax, same λ~650 nm

Ag

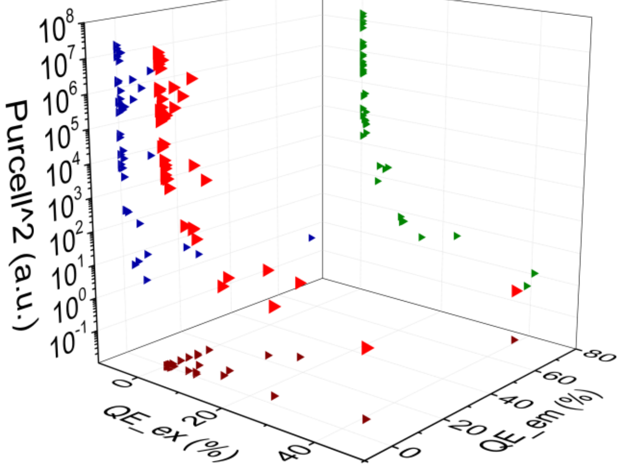
scattering Gmax-LMax ~ Purcell*QE Lmax-Gmax, same λ~532–650 nm

extinction Gmax-LMax ~ Purcell Lmax_1-Lmax_2, same λ~532–650 nm

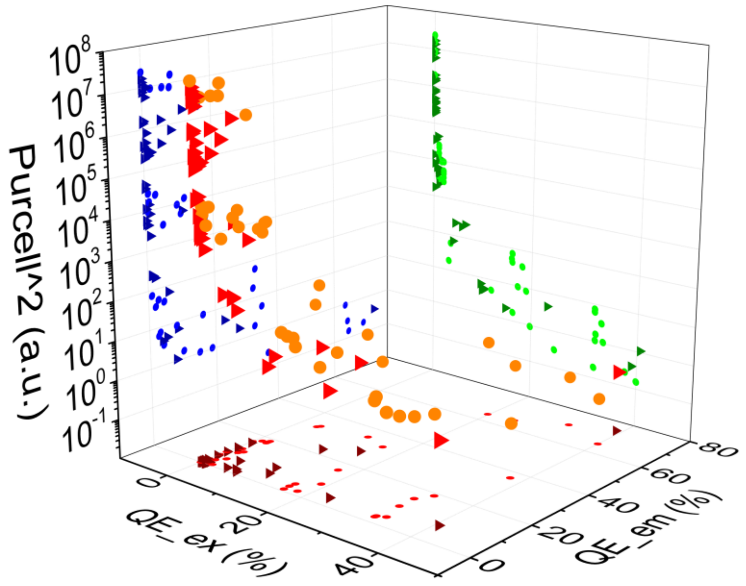
Coincident peaks in optical response and scattering cross-section at 650/532-650 nm in case of Au/Ag nanorod

Fluorescence enhancement of SiV color centers with gold nanorod (532-738 nm)

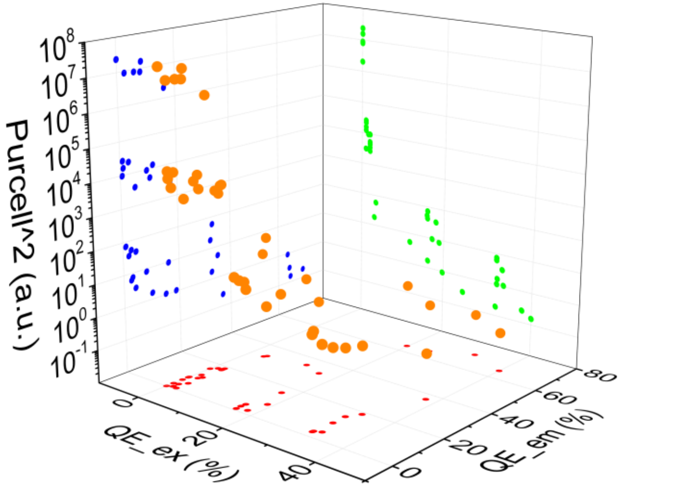
Perpendicular dipoles!



QE maximization with Purcell criterion



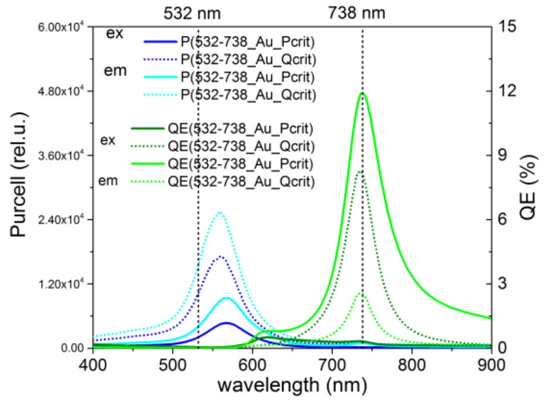
Integrated 3D parameter curve

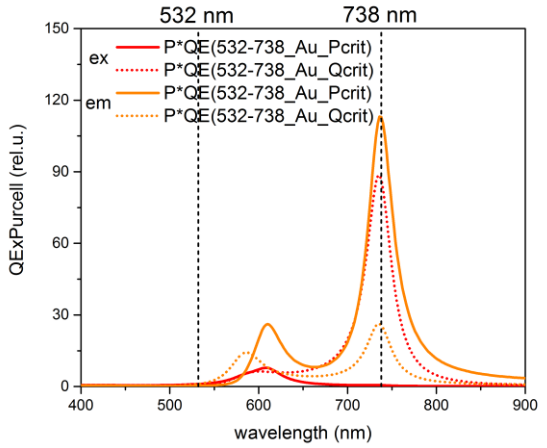


Purcell maximization with QE criterion

<u>wavelength dependence of optical responses in selected configurations:</u>

- wide distribution similarly to configurations optimized for 738 nm for single wavelength
- gap is observable in case of Pcrit again
- Pcrit works well in region of large Purcell values



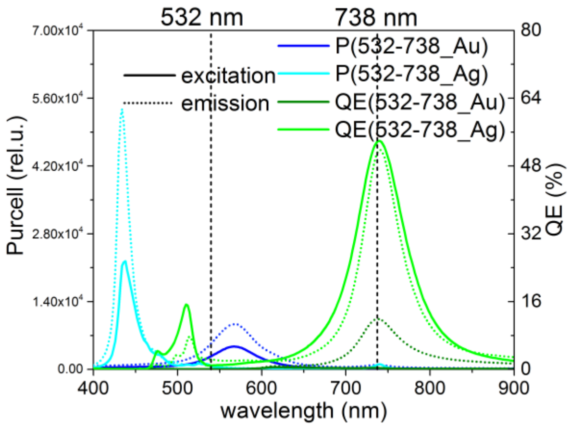


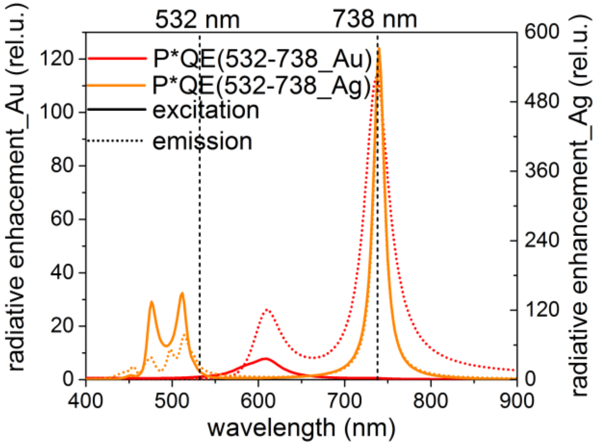
<- local Purcell and global QE and P*QE maxima at 738 gold results in small enhancement at 532

Optical response and cross-sections of selected gold and silver nanorod configurations at SiV emission and excitation wavelength (532-738 nm)

532-738	Purcell (rel.u.) excitation	QE (%) excitation	Purcell·QE (a.u.) excitation	Purcell (rel.u.) emission	QE (%) emission	Purcell·QE (a.u.) emission	(Purcell·QE)^2	long axis (nm)	short axis (nm)	aspect ratio	dipole distance (nm)	inclination (°)
Au	1848.31	0.06	1.04	949.02	11.9	112.93	117.23	58.92	38.2	1.54	2.94	40.2 | -49.8
Ag	1001.2	3.1	31.05	1347.81	52.8	711.71	22099.52	62.86	33.52	1.88	2.16	-11.01
Ag/Au	0.54	55.22	29.91	1.42	4.44	6.3	188.52	1.07	0.88	1.22	0.73	0.27

Optical response





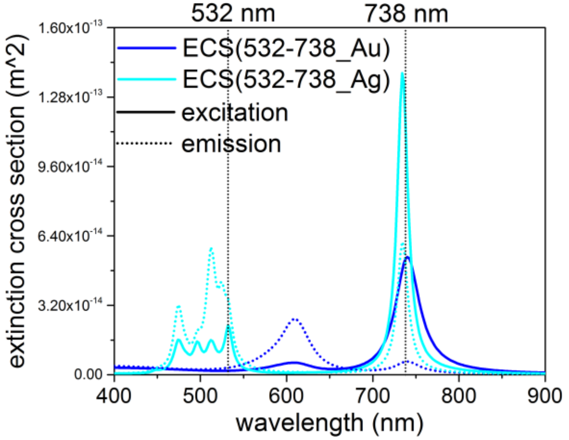
Considerable excitation and emission enhancement achievable via both nanorods, silver is better

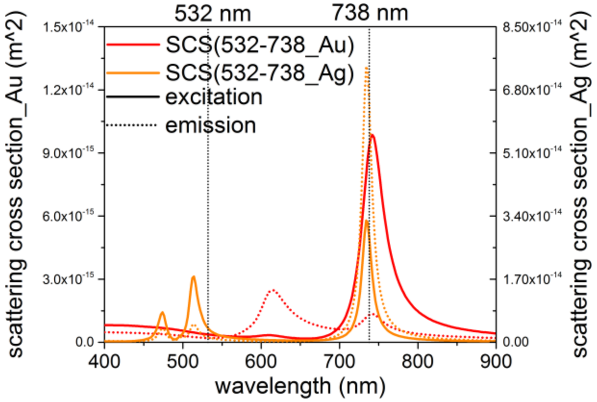
Au

scattering Lmax-Gmax ~ Purcell*QE Lmax-Gmax, same λ >532 nm - ~738 nm

extinction Lmax-Gmax ~ Purcell Gmax-Lmax, same λ >532 nm - ~738 nm

Scattering cross-sections





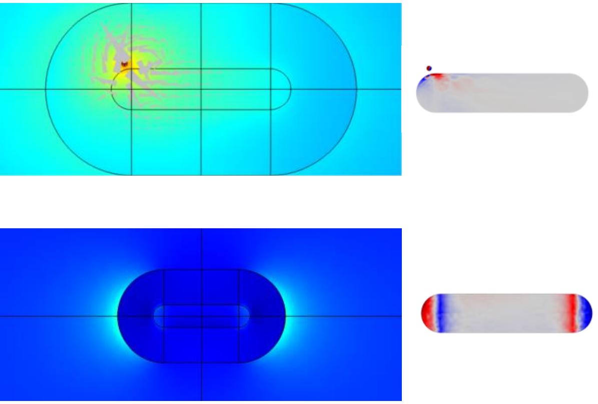
Ag

scattering Lmax-Gmax ~ Purcell*QE Lmax-Gmax, same λ~532–738 nm

extinction Lmax-GMax ~ Purcell Gmax-Lmax, same λ~532–738 nm

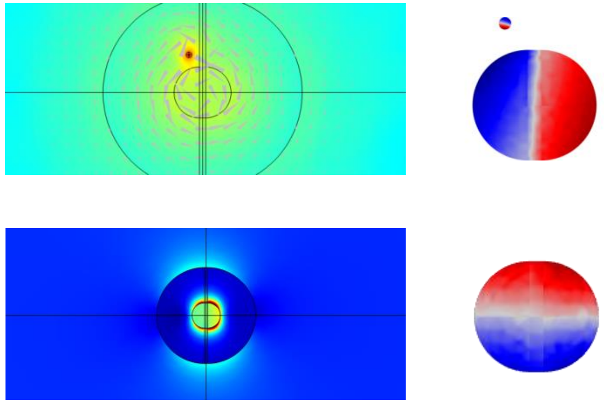
Coincident peaks in optical response and scattering cross-section at <532-738 nm in case of both nanorods

532_Au



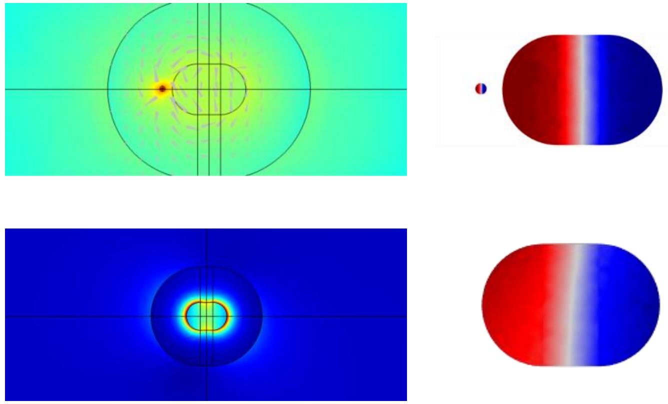
Surface dipole – surface quadrupole

650_Au



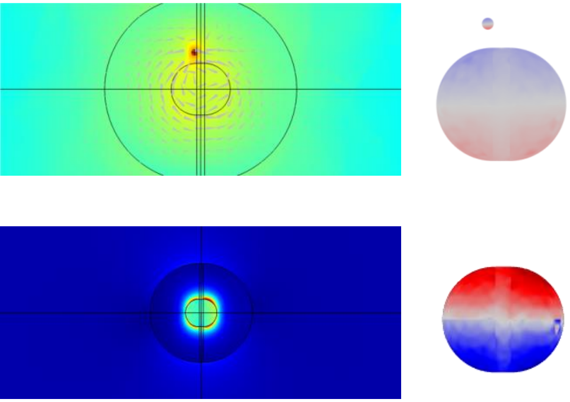
Volume dipole of different orientation

738_Au



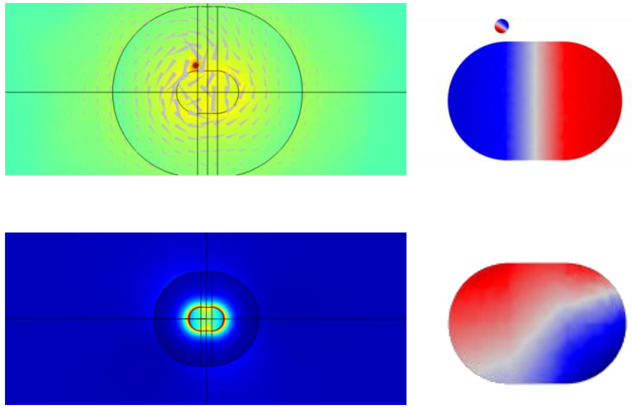
Volume dipoles of analogous orientation

532_Ag



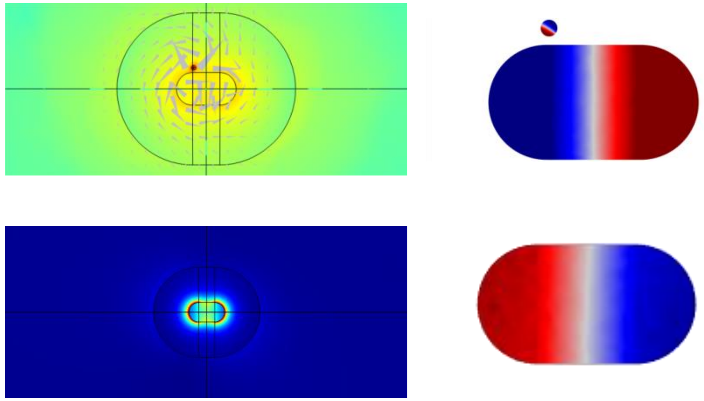
Volume dioles of different orientation

650_Ag

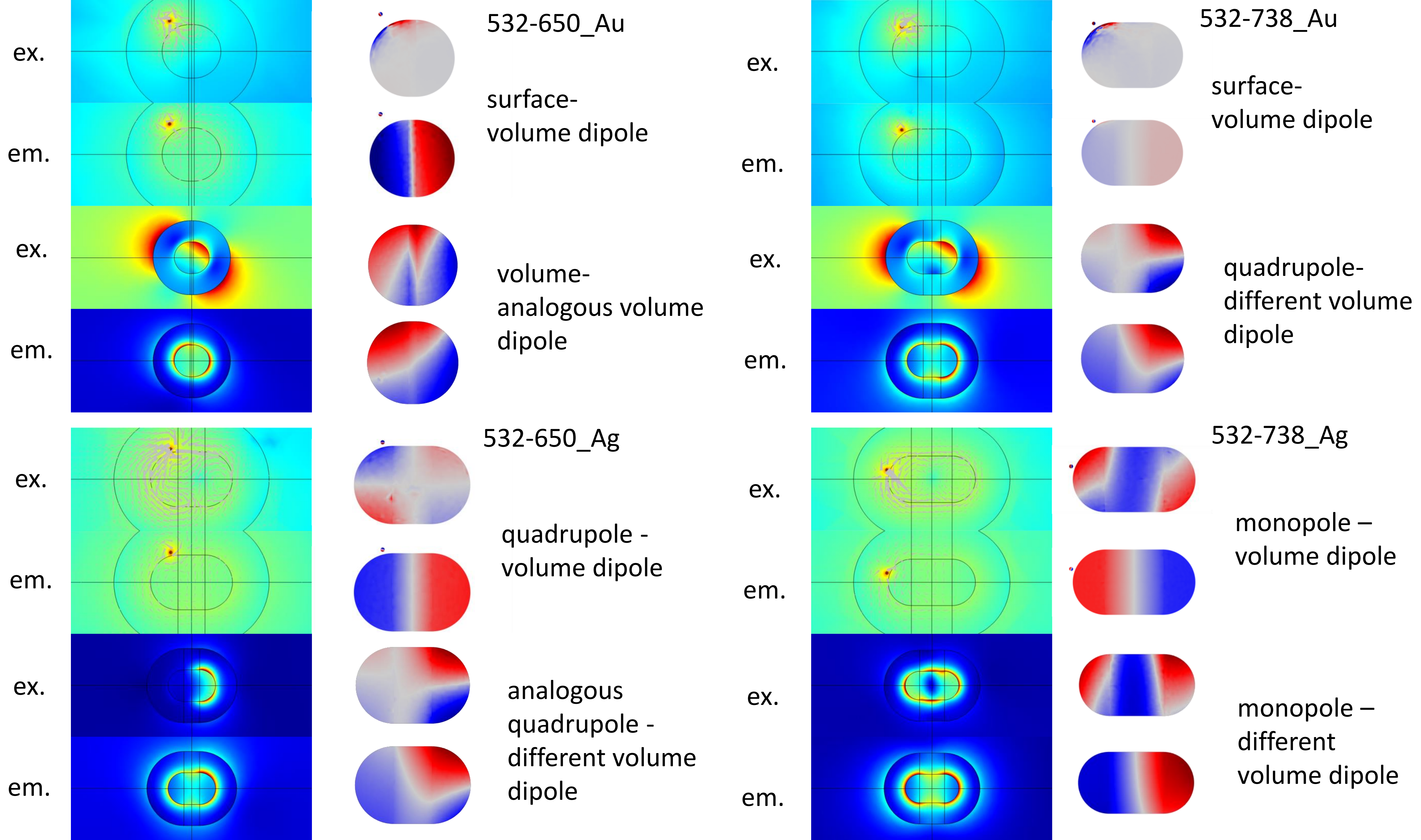


Volume dipoles of analogous orientation

738_Ag



Volume dipoles of different orientation


532-650_Au
ex.
em.
ex.
em.
surface-
volume dipole
volume-
analogous volume
dipole
532-738_Au
ex.
em.
ex.
em.
surface-
volume dipole
quadrupole-
different volume
dipole
532-650_Ag
ex.
em.
ex.
em.
quadrupole -
volume dipole
analogous
quadrupole -
different volume
dipole
532-738_Ag
ex.
em.
ex.
em.
monopole –
volume dipole
monopole –
different
volume dipole

Conclusion

Single wavelength optimization
532 nm
-Au cannot result in enhancement, no corresponding peaks on cross-sections
-Ag results in enhancement, corresponding maxima on SCS and ECS
650 nm and 738 nm
-Au / Ag results in small / large enhancement, corresponding maxima on SCS ad ECS

Dual wavelength optimization
532 nm - 650 nm and 532 nm – 738 nm
-Au results in emission enhancement, corresponding maxima on SCS and ECS
-Ag results in excitation and larger emission enhancement, corresponding double maxima on SCS and ECS

Optimal configurations cannot be predicted based on plane-wave illumination,
Optimization is indispensable, and the right criteria and objective function combination depends on the type of the plasmonic resonator.

Acknowledgements

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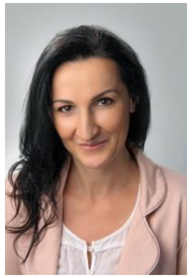

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A. Szenes, B. Bánhelyi, L. Zs. Szabó, G. Szabó, T. Csendes, M. Csete: "*Enhancing diamond color center fluorescence via optimized plasmonic nanorod configuration*", Plasmonics, DOI: 10.1007/s11468-016-0384-1