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

(a) 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

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

\[ \gamma_{\text{excitation}} / \gamma_0^{\text{excitation}} = \left| \frac{p \cdot E}{p_0 \cdot E_0} \right| \]

reciprocity theorem

\[ \frac{\gamma^{\text{radiative}}}{\gamma_0^{\text{emission}}} = \frac{QE}{QE_0^{\text{emission}}} \cdot \frac{\gamma^{\text{radiative}}}{\gamma_0^{\text{excitation}}} \]

2. Purcell effect

- \( \tau \) modifies in inhomogeneous environment
- relative enhancement is described by:

\[ \text{Purcell} = \frac{p_{\text{total}}}{p_0^{\text{total}}} = \frac{p^{\text{radiative}}}{p_0^{\text{radiative}}} + \frac{p^{\text{non-radiative}}}{p_0^{\text{non-radiative}}} \]

Excitation enhancement can be described with Purcell!

\[ \tau = 1 / \Gamma \]

3. Antenna effect

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

\[ QE = \frac{p^{\text{radiative}}}{p_{\text{total}}} \]

Approach for diamond color centers’ fluorescence enhancement via metal nanoparticles

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

Designing nanorods capable of enhancing fluorescence at “arbitrary” wavelengths

Geometry optimization via COMSOL

External in-house made optimization algorithm: GLOBAL

- electric point dipole
- materials
- read-out surfaces

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

Trade-off between Purcell and QE

Conditional optimization

- Purcell condition
- OR?
- QE condition

Single λ

Dual λ

Purcell_excitation & Purcell_emission conditions

OR?

QE_excitation & QE emission conditions
Modelling and comparative study on scattering cross-section extracted from 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

wavelength dependence of optical responses in selected configurations:

- optimized configurations on the same curve, but in significantly different regions
- $P_{crit}$ shows more configurations in large Purcell region
- $Q_{crit}$ makes it possible to operate with large QE
Considerable excitation enhancement achievable via silver nanorod

Optical response

scattering different tendency, coincident $L_{\text{max}}$: $\lambda \sim 720$ nm

extinction $L_{\text{max}} \sim \text{Purcell}$ $L_{\text{max}}$: same $\lambda \sim 720$ nm

Ag

Scattering cross-sections

scattering $G_{\text{max}} \sim \text{Purcell} \times \text{QE}$ $G_{\text{max}}$, same $\lambda \sim 532$ nm

extinction $G_{\text{max}} \sim \text{Purcell} L_{\text{max}}$, same $\lambda \sim 532$ nm

Ag

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

<table>
<thead>
<tr>
<th>532</th>
<th>Purcell (rel.u.)</th>
<th>QE (%)</th>
<th>Purcell-QE (a.u.)</th>
<th>long axis (nm)</th>
<th>short axis (nm)</th>
<th>aspect ratio</th>
<th>dipole distance (nm)</th>
<th>Inclination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>5306.18</td>
<td>0.03</td>
<td>0.96</td>
<td>68.44</td>
<td>15.54</td>
<td>4.4</td>
<td>2.34</td>
<td>74.09</td>
</tr>
<tr>
<td>Ag</td>
<td>1076.43</td>
<td>6.06</td>
<td>0.32</td>
<td>35.21</td>
<td>19.37</td>
<td>1.15</td>
<td>4.16</td>
<td>7.97</td>
</tr>
<tr>
<td>Ag/Au</td>
<td>0.36</td>
<td>190.25</td>
<td>0.32</td>
<td>38.12</td>
<td>1.25</td>
<td>0.26</td>
<td>1.78</td>
<td>0.11</td>
</tr>
</tbody>
</table>
Emission enhancement of NV color centers with gold nanorod (650 nm)

- QE maximization with Purcell criterion
- Purcell maximization with QE criterion

Integrated 3D parameter curve

Wavelength dependence of optical responses in selected configurations:

- 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)

Considerable emission enhancement achievable via both nanorods, silver is better.

Optical response

Scattering cross-sections

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

<table>
<thead>
<tr>
<th>650</th>
<th>Purcell (rel.u.)</th>
<th>QE (%)</th>
<th>Purcell-QE (a.u.)</th>
<th>long axis (nm)</th>
<th>short axis (nm)</th>
<th>aspect ratio</th>
<th>dipole distance (nm)</th>
<th>inclination (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>1002.01</td>
<td>0.94</td>
<td>9.42</td>
<td>20</td>
<td>17.81</td>
<td>1.12</td>
<td>4.78</td>
<td>-8.36</td>
</tr>
<tr>
<td>Ag</td>
<td>9262.95</td>
<td>4.73</td>
<td>438.16</td>
<td>24.28</td>
<td>16.51</td>
<td>1.47</td>
<td>2.18</td>
<td>18.91</td>
</tr>
<tr>
<td>Ag/Au</td>
<td>9.24</td>
<td>5.03</td>
<td>46.5</td>
<td>1.21</td>
<td>0.93</td>
<td>1.31</td>
<td>1.46</td>
<td>2.26</td>
</tr>
</tbody>
</table>

scattering $L_{\text{max}} \sim \text{Purcell}\cdot\text{QE}$ $G_{\text{max}}$, same $\lambda \sim 650$ nm

extinction $L_{\text{max}} \sim \text{Purcell}$ $L_{\text{max}}$ same $\lambda \sim 650$ nm

Au

Ag

650

Purcell (rel.u.)

QE (%)

Purcell-QE (a.u.)

long axis (nm)

short axis (nm)

aspect ratio

dipole distance (nm)

inclination (°)

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

- QE maximization with Purcell criterion
- Purcell maximization with QE criterion

Integrated 3D parameter curve

Wavelength dependence of optical responses in selected configurations:
- 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
Considerable emission enhancement achievable via both nanorods, silver is better

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

<table>
<thead>
<tr>
<th>738 nm</th>
<th>Purcell (rel.u.)</th>
<th>QE (%)</th>
<th>Purcell-QE (a.u.)</th>
<th>long axis (nm)</th>
<th>short axis (nm)</th>
<th>aspect ratio</th>
<th>dipole distance (nm)</th>
<th>inclination (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>2.15</td>
<td>2.15</td>
<td>44.14</td>
<td>28.45</td>
<td>19.56</td>
<td>1.45</td>
<td>3.8</td>
<td>-23.39</td>
</tr>
<tr>
<td>Ag</td>
<td>5.58</td>
<td>1548.08</td>
<td>25.05</td>
<td>13.73</td>
<td>2</td>
<td>48.1</td>
<td>48.1</td>
<td></td>
</tr>
<tr>
<td>Ag/Au</td>
<td>2.59</td>
<td>0.88</td>
<td>35.07</td>
<td>0.7</td>
<td>1.25</td>
<td>0.53</td>
<td>2.06</td>
<td></td>
</tr>
</tbody>
</table>

**Optical response**
- Scattering $L_{max} \sim$ Purcell*QE $G_{max}$, same $\lambda=738$ nm
- Extinction $L/G_{max} \sim$ Purcell $G/L_{max}$, same $\lambda<\lambda=738$ nm

**Scattering cross-sections**
- Scattering $G_{max} \sim$ Purcell*QE $G_{max}$, same $\lambda \sim 738$ nm
- Extinction $G_{max} \sim$ Purcell $G_{max}$, same $\lambda \sim 738$ nm
Fluorescence enhancement of NV color centers with gold nanorod (532-650 nm)

Integrated 3D parameter curve

wavelength dependence of optical responses in selected configurations:

- gaps in both optimization methodologies
- $P_{\text{crit}}$ still supports large Purcell and small QE
- $Q_{\text{crit}}$ more points in QE [80,100] interval: local search

<- local Purcell and global QE & $P^*Q_E$ maxima at 650 gold nanorod does not result 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)

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

Optical response

Scattering cross-sections

Coincident peaks in optical response and scattering cross-section at 650/532-650 nm in case of Au/Ag nanorods
Fluorescence enhancement of SiV color centers with gold nanorod (532-738 nm)

QE maximization with Purcell criterion

Integrated 3D parameter curve

wavelength dependence of optical responses in selected configurations:

- 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

Perpendicular dipoles!
Considerable excitation and emission enhancement achievable via both nanorods, **silver** is better

**scattering** \( L_{\text{max}} - G_{\text{max}} \sim \text{Purcell} \times \text{QE} \) \( L_{\text{max}} - G_{\text{max}} \), same \( \lambda > 532 \text{ nm} \) - \( \sim 738 \text{ nm} \)

**extinction** \( L_{\text{max}} - G_{\text{max}} \sim \text{Purcell Gmax-Lmax} \), same \( \lambda > 532 \text{ nm} \) - \( \sim 738 \text{ nm} \)

Coincident peaks in optical response and scattering cross-section at <532-738 nm in case of both nanorods
Surface dipole – surface quadrupole

Volume dipole of different orientation

Volume dipoles of analogous orientation

Volume dipoles of different orientation

Volume dipoles of analogous orientation

Volume dipoles of different orientation
ex. 532-650_Au  

em. surface-volume dipole

ex. volume-analogous volume dipole

em. 532-650_Ag  

ex. quadrupole - volume dipole

em. analogous quadrupole - different volume dipole

em. 532-738_Au

em. surface-volume dipole

ex. quadrupole - different volume dipole

em. 532-738_Ag

em. monopole - volume dipole

em. 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 and 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.
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