Plasmon-Exciton Interactions in Bilayers of Core-Shell Au-SiO_2 Nanoparticles and $FAPbI_3$ Perovskite Nanocrystals

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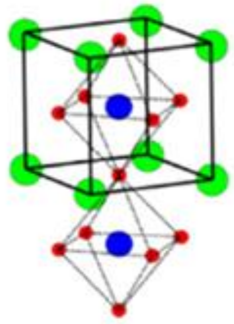
Motivation



- Metal Halide Perovskites (MHPs): Outstanding optoelectronic materials, competing against established semiconductors (silicon) mainly in solar cells, but also in other photonic applications and devices

- Much of the early work performed on the prototype MHP material $MAPbI_3$ but more recent work focuses on $FAPbI_3$-based structures due to its narrower bandgap and better thermal durability

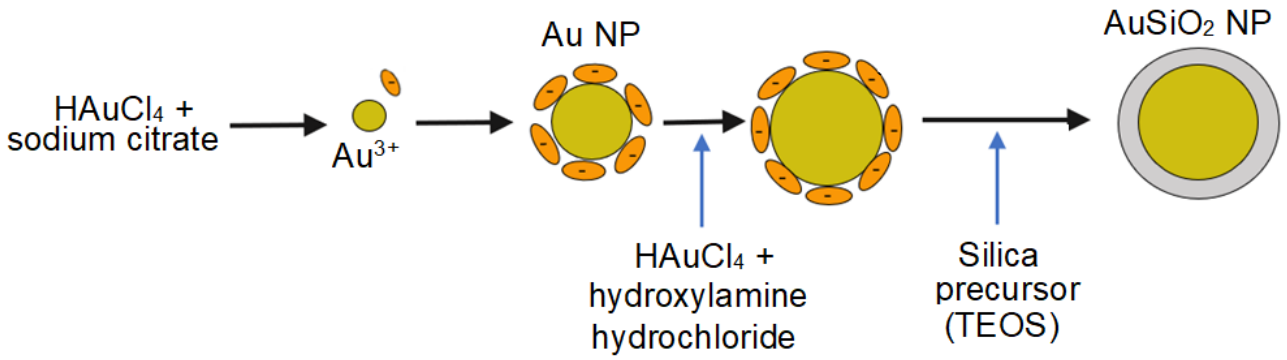
- $FAPbI_3$ in the form of colloidal nanocrystals (NCs) shows increased structural integrity compared to bulk, due to surface ligand coverage

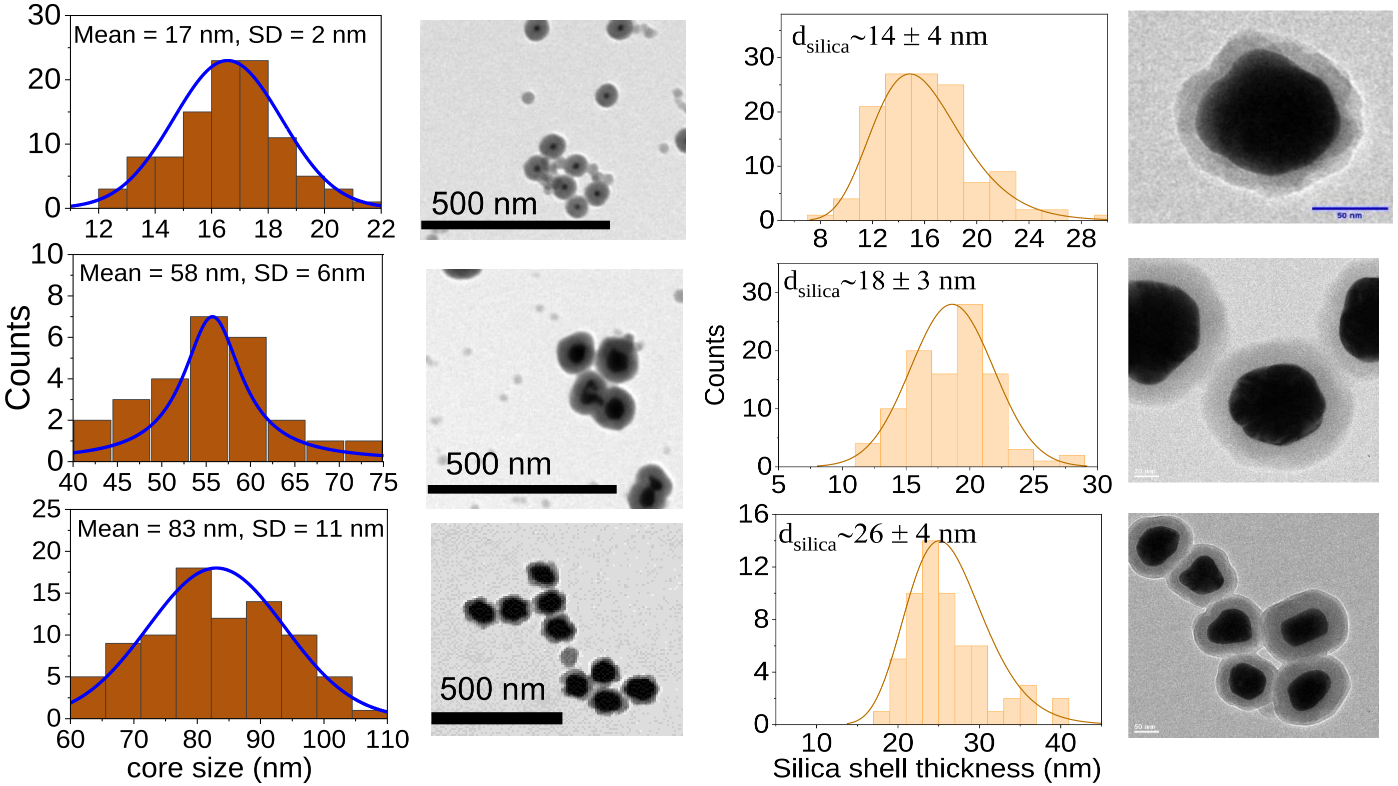
- An issue associated with $FAPbI_3$ is the drop of absorption coefficient above ~500 nm. In NCs absorption reduces further due to a smaller density of states and a reduced solid state packing due to ligands

- An obvious solution is to use thicker $FAPbI_3$ absorbers, but this leads to disorder and unfavourable competition of the carrier extraction with non-radiative recombination

❖ Alternative approach in this work: Implement plasmonic $AuSiO_2$ nanoparticles (NPs) of tunable core and shell size to optimize near- and/or far field plasmon/light-exciton interaction and obtain enhanced light harvesting efficiency

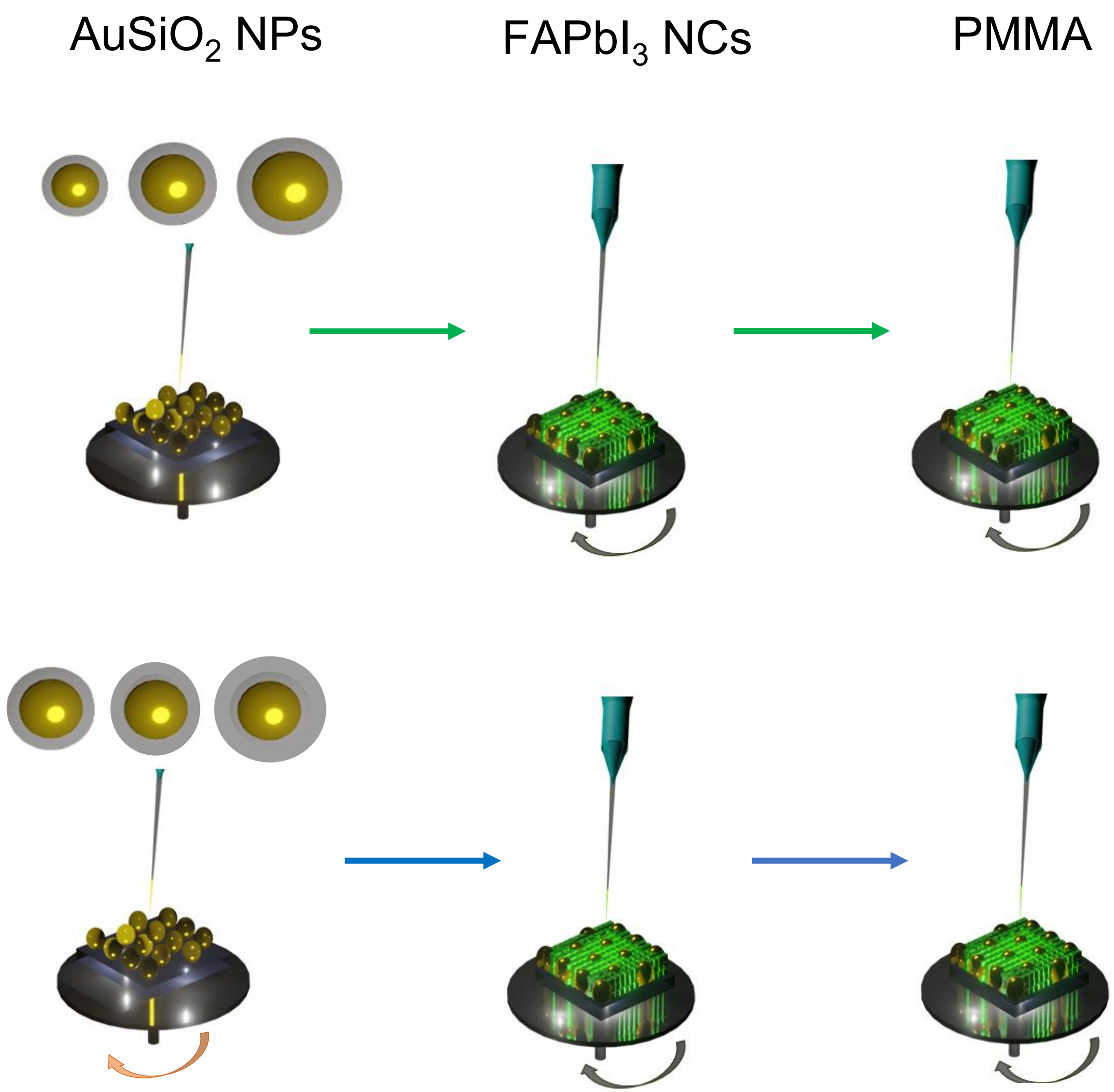
Synthesis of $AuSiO_2/FAPbI_3$ NPs of tunable core/shell size





- Synthesis of 15, 40 nm Au NPs based on the modified Frens method [1][2]
- Growth of 60 and 80 nm Au NP [1]
- Core sizes of 17 ± 2, 58 ± 6, 83 ± 11 nm with shell size ~ 20-25 nm
- Silication via the Stöber method with various amounts of silica precursor [2][3]
- Shell sizes: 14 ± 4, 18 ± 3 and 26 ± 4 nm

Fabrication of $AuSiO_2/FAPbI_3$ bilayers



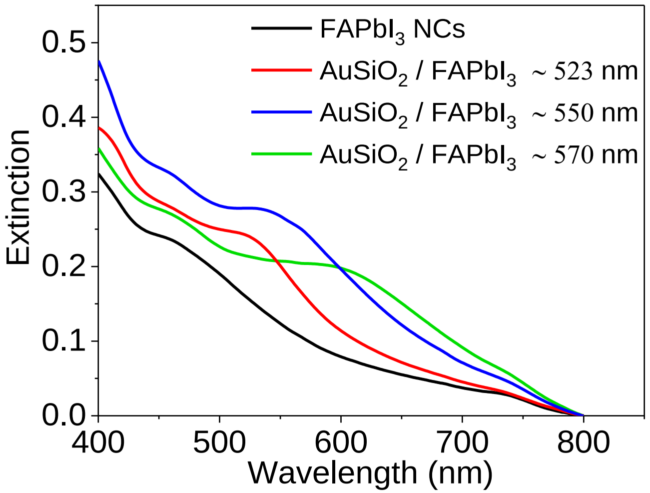
Core-size dependent study:

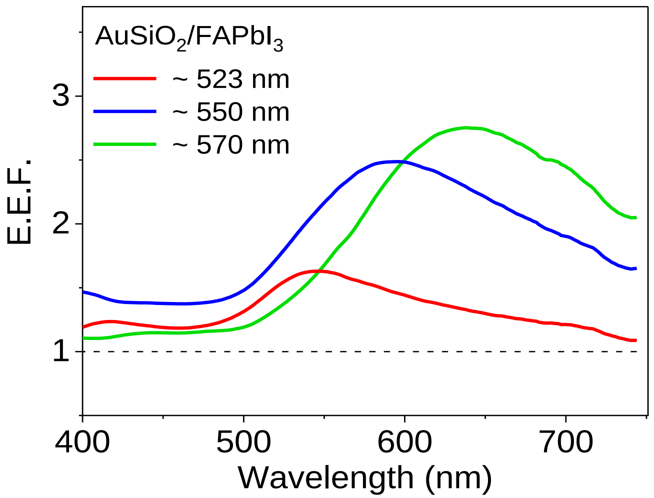
- Drop-cast $AuSiO_2$ NPs in ethanol on glass substrates and vacuum dry (thick layer)
- Spin-cast $FAPbI_3$ NCs, followed by PMMA

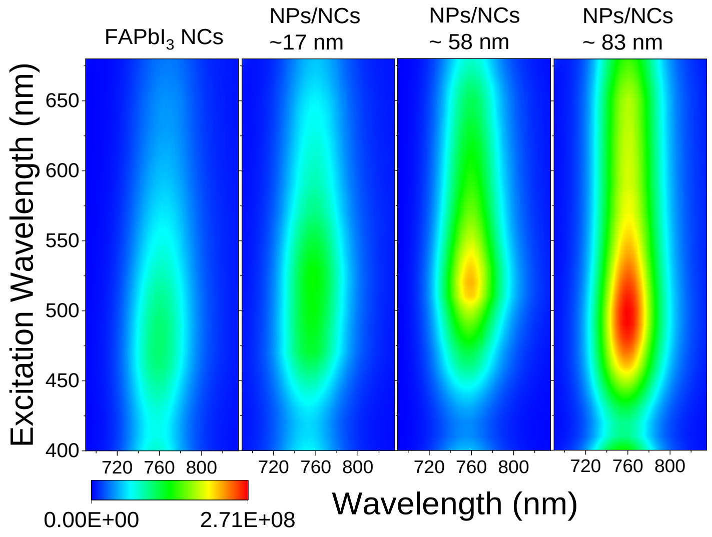
Shell-size dependent study:

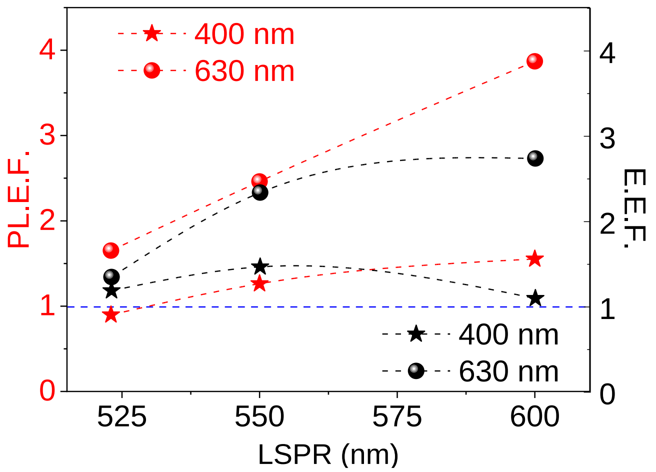
- Spin-cast $AuSiO_2$ NPs in ethanol on poly-L-lysine coated glass substrates (thin layer)
- Spin-cast $FAPbI_3$ NCs, followed by PMMA

Impact of Au core size on optical properties of $AuSiO_2/FAPbI_3$ bilayers



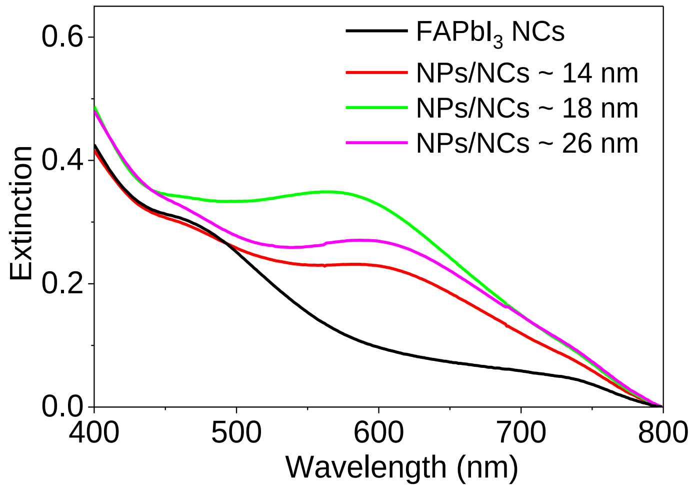


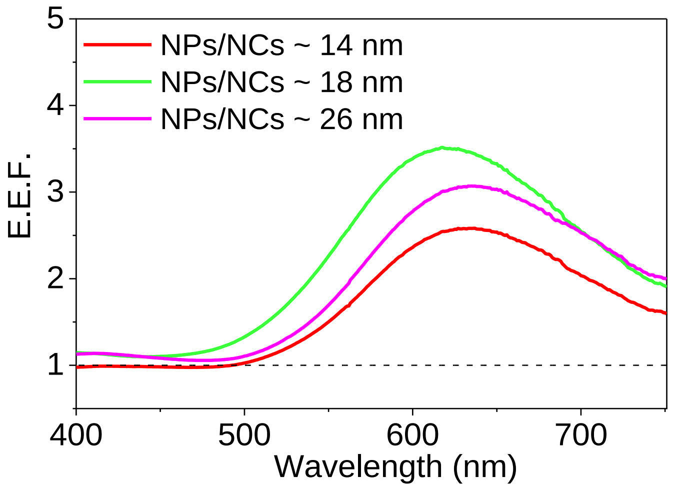


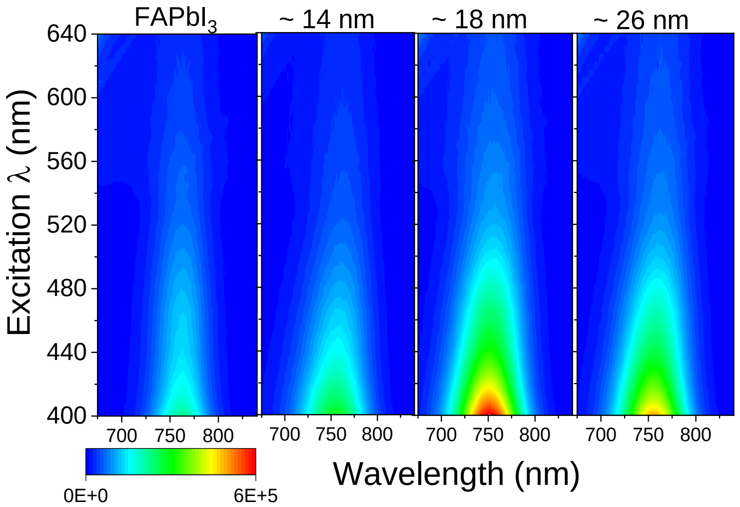


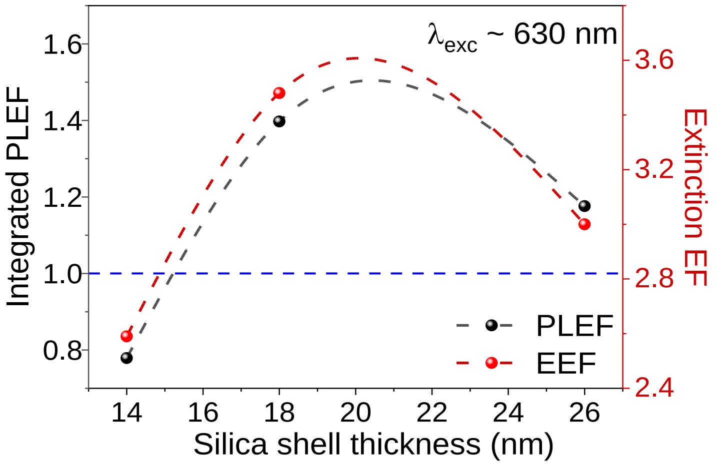
- Au NP size dependent enhancement of extinction by the near and far-field effects
- Emission enhancement which traces the spectral variation of extinction spectra
- Strongest emission from the largest Au NPs, due to combination of stronger near-field coupling and more efficient far-field scattering

Impact of silica shell size on optical properties of $AuSiO_2/FAPbI_3$ bilayers



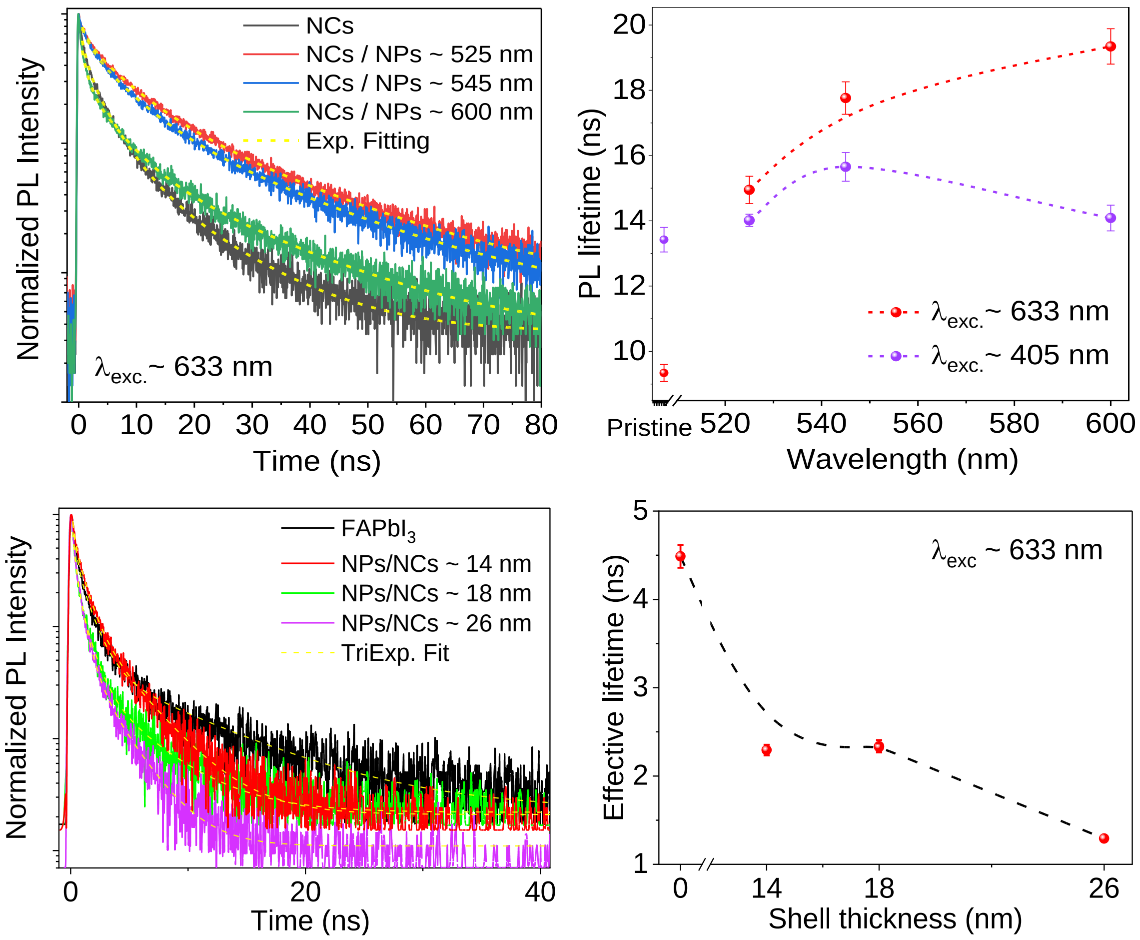






- Shell-size dependent extinction enhancement, maximizing for the 18 nm shell
- Emission enhances for all bilayers at off resonance excitation (<500 nm), by far-field interactions
- At on resonance excitation (>500 nm), emission quenches for the smallest shell size and enhances for the larger ones
- Emission enhancement maximizes at the 18 nm shell consistent with extinction enhancement and theoretical predictions

Plasmon-exciton interaction mechanisms



$$\tau_{Ex-Pl} = \frac{1}{k_{r,0} + k_{nr,0} + k_{RET} + k_{Pur}}$$

Core size study:

- Lengthening of lifetime with Au NP size implies dominance of far-field effects (photon recycling)
- High NP-NC separation distance due to film thickness reduces near-field interaction contribution

Shell size study:

- Quenching of lifetimes at on resonance excitation implies dominance of near-field effects due to small NP-NC separation distance
- Resonance energy transfer responsible for emission/lifetime quenching at 14 nm shell size
- The Purcell effect responsible for the emission enhancement and lifetime quenching at larger shell sizes

References

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Thank you