DISTANCE DEPENDENT FLUORESCENCE QUENCHING BY GOLD NANOSTRUCTURES

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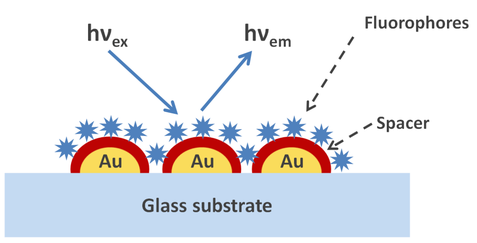
Background and objective

Nanostructured metal (e.g., gold, silver) surfaces support **localized surface plasmon resonance** (**LSPR**) charge-density oscillations, exhibited as an optical extinction band. The LSPR band shifts in both wavelength and intensity in response to adsorption of dielectric materials. The response depends on the thickness of the coating, becoming weaker for thicker coatings, due to the decay of the plasmon evanescent field. We have previously shown, using a variety of gold nanoisland films, that **the LSPR decay length is directly related to the size of the gold nanoislands**:[1] while the decay length of small islands is of the order of a few nanometers, that of large islands reaches tens of nm.

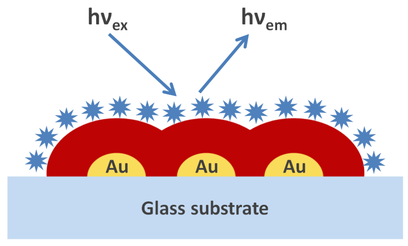
Plasmonic nanoparticle films interact with fluorescent species, quenching or enhancing the fluorescent emission ("*metal enhanced fluorescence*"), depending, among other factors, on the spacing between the metal structure and the fluorophore.

Question: ***Is the distance dependence of metal enhanced fluorescence related to the plasmon decay length?***

Concept



Gold islands / thin spacer / fluorophore



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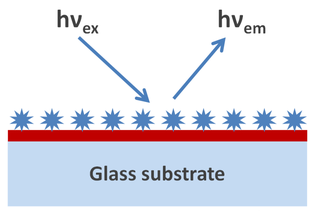
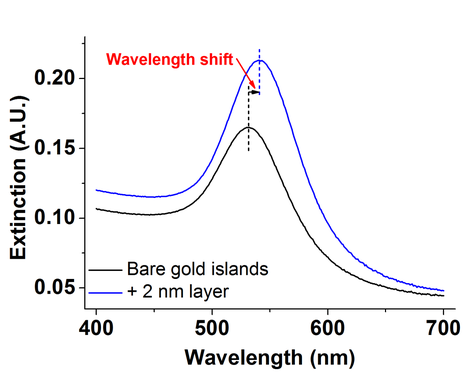
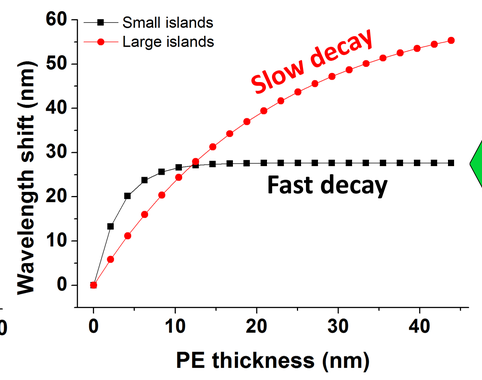


Control: glass / adhesion layer / fluorophore

Two types of Au nanoisland films were used, of ~20 and ~100 nm average diameter. Fluorescence intensity measured as a function of metal-fluorophore separation, compared to intensity from fluorophore on inert substrate as a control.

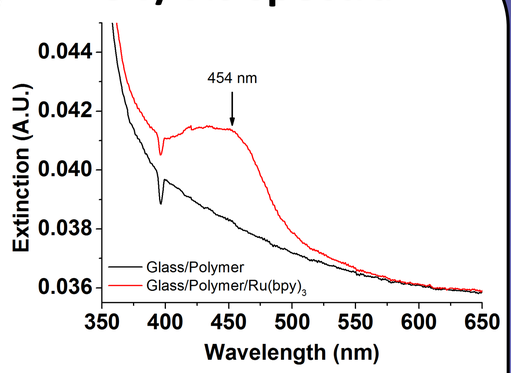
LSPR peak response to spacer thickness





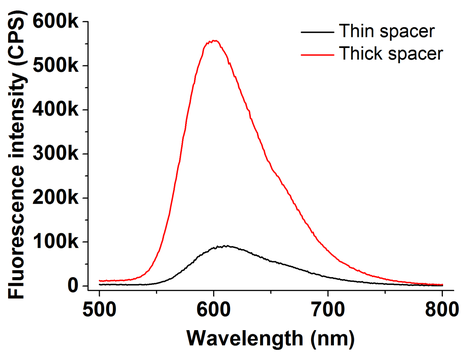
Shift of the LSPR peak wavelength upon adsorption of a dielectric layer of increasing thickness. The response decays rapidly for small islands (no change after ~10 nm) and slowly for large islands (the peak shifts even after 40 nm).

UV/Vis spectra



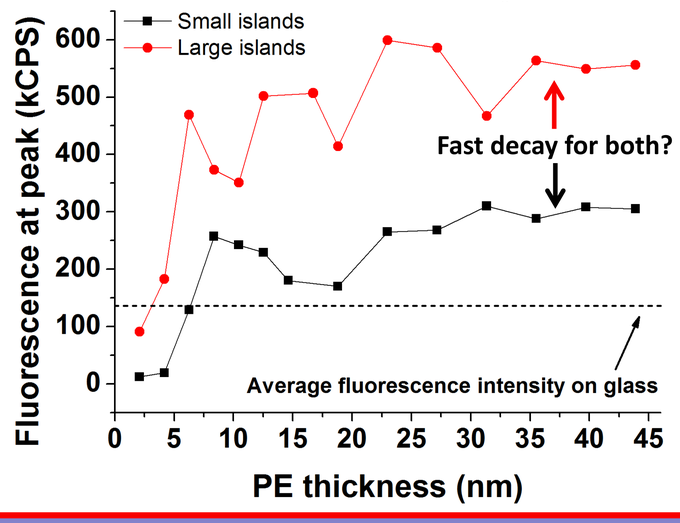
Peak intensity varies by <20% for 9 slides, showing the repeatability of the adsorption method.

Fluorescence quenching



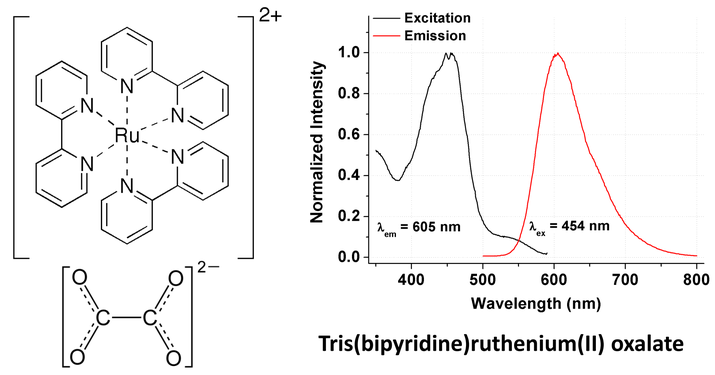
For thin spacers, the fluorescence is strongly quenched. Fluorescence intensity on large islands, for spacer layers 2.1 nm and 44.1 nm thick.

Fluorescence distance dependence



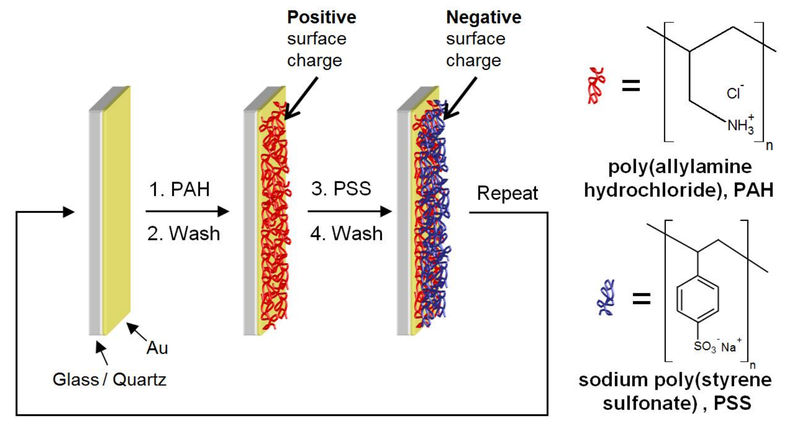
The system

Fluorophore: $Ru[bpy]_3^{2+}$



Tris(bipyridine)ruthenium(II) oxalate

Polyelectrolyte (PE) spacer

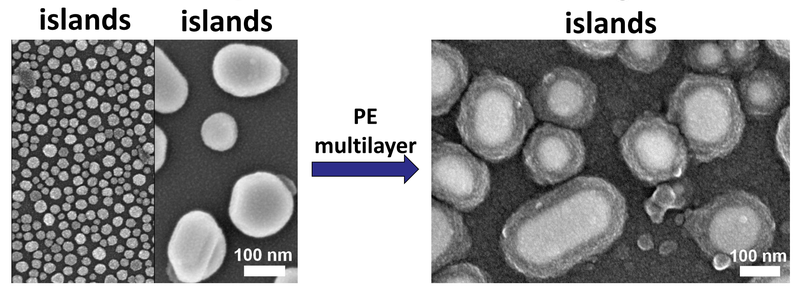


Each PAH/PSS bilayer is 2.09 ± 0.03 nm thick
(measured by spectroscopic ellipsometry; n = 1.56 in the visible range)
Adsorption solution: 1 mM (monomer) polyelectrolyte in 0.1 M aqueous NaCl; 15 min per deposition step.

Fluorophore binding

The top layer of the polyelectrolyte multilayer spacer is the negatively-charged PSS, to which the positively charged fluorescent ruthenium complex binds electrostatically. In the control slides the glass is first functionalized with 3-aminopropyl trimethoxysilane creating a positive surface charge, followed by electrostatic binding of PSS.

Gold nano-islands and PE coating



High-resolution SEM images of Au island films thermally evaporated on glass slides and annealed 10 h at 580 °C. Left: samples of 3 nm and 10 nm nominal thickness; right: 10 nm (nominal thickness) islands, coated with 40 polyelectrolyte layers. In-Lens SE detector, 10-20 kV; coated with 2-3 nm Cr.

Analysis

- At short range (few nm) the fluorescence is strongly quenched, due to energy transfer from excited fluorophores to the nanoislands. At longer range, fluorescence is enhanced (vs. controls).
- The distance profile seems similar for both island types, despite the different LSPR decay lengths; this conclusion is questionable due to the large experimental scatter.
- The enhancement is different for the two types, ca. 3-fold for small islands and 6-fold for large islands.
- No enhancement peak is seen, i.e., the intensities do not decrease to the control level even at large separations.

Future directions

- Reduce experimental scatter.
- Is the surface coverage for the controls and different gold islands the same?
- Effect of overlap between emission or excitation peaks and LSPR peak.
- Effect on fluorescence lifetimes.
- Use of larger separations.

[1] Kedem, O.; Tesler, A. B.; Vaskevich, A.; Rubinstein, I. Sensitivity and Optimization of Localized Surface Plasmon Resonance Transducers, *ACS Nano* **2011**, *5*, 748-760.