Plasmonic interactions of gold nanoparticles with photoluminescent materials

Carolyn Elliott, School of Physics, Trinity College Dublin, 2024

Abstract

The variable plasmonic resonances of metal nanoparticles have many applications across a wide range of fields, including the modification of the emission of photoluminescent materials. The plasmonic interactions of gold nanoparticles with two types of photoluminescent nanoparticles are explored. Plasmonic gold nanoparticles are synthesised: nanorods, bipyramids, and nanostars. The concentration of the reagents used in their syntheses are varied to produce nanoparticles with both sharp and broad plasmon resonances across the visible and near infrared spectrum, from 600 nm to above 1100 nm. The particles are also simulated, to observe the electric field enhancements of each particle type. A full investigation into the effect of varying the concentration of the reducing agent, l-ascorbic acid, in the synthesis of bipyramids is carried out. A nonlinear dependence is found, with a sharp increase at lower l-ascorbic acid concentrations and a plateau at higher concentrations, likely due to the change in ratio between l-ascorbic acid and $HAuCl_4$. Bipyramids with plasmon resonance wavelengths longer than 1000 nm are synthesised without the use of a regrowth step[1,2] or reducing seed concentration[3], but by only varying AA concentration, which has not been previously achieved in the literature.

Using the high electric field enhancements and small mode volume of the gold bipyramids, plasmon-induced two-photon polymerisation is shown. Polymerisation is demonstrated at powers far below the threshold typically required, as the bipyramids enhance the electric field of incoming laser light. A linear relationship between polymerised area (visible from SEM) and applied laser power is discovered, further corroborating this enhancement as the polymerised area depends on the electric field strength.

This enhanced polymerisation allows for spatial confinement of quantum dots. When quantum dots are added to the monomer, they remain wherever the solution is polymerised, and all other quantum dots are removed. They are trapped at the location of highest field enhancement, by design, and thus

also interact with the plasmonic bipyramid. This provides a novel fabrication method for bipyramid-quantum dot pairs, with quantum dots preferentially confined at one tip of a bipyramid. The localisation of the quantum dots in this high field enhancement area results in emission rate enhancement and even strong coupling between the quantum dots and bipyramids, shown by Rabi splitting in the bipyramid scattering spectra.

Upconverting nanoparticles of various sizes, dopants, and emission wavelengths are synthesised. The dopants, Yb^{3+}, Er^{3+} and Tm^{3+}, give emission wavelengths from 450-800 nm and the sizes obtained by varying synthesis reaction volume and the speed of injecting the nucleation solution were between ≈ 5-40 nm. Layer-by-layer deposition of these particles is carried out, resulting in samples with even and consistent upconversion emission. These are topped with polyelectrolyte spacer layers followed by nanostars, nanorods and bipyramids, resulting in enhancement by nanorods and bipyramids, with bipyramid enhancement of up to 7.5x, the first time such enhancement has been demonstrated.

In order to create samples with higher plasmonic nanoparticle concentrations, spin-coating is employed. Multiresonant gold nanostars, coated with silica shells as spacers, are spin-coated atop upconverting nanoparticle layers. Samples with high nanostar concentration demonstrate enhancement, with nanostar clusters showing enhancement of up to 9.7x. This high enhancement value likely occurs due to plasmonic hotspots between the nanostars, and could have applications in the enhancement of upconverting nanoparticle emission for use in solar cell efficiency improvement[4,5].