Analytical formulation for field enhancement of gold bipyramids and hemispherically capped cylinders for application in two-photon luminescence and scattering

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Recent advances in two-photon excited photoluminescence of plasmonic gold nanorods have greatly expanded their application. Shape-controlling of nanorods can enhance a particular photophysical process to tailor needs but its application to two-photon luminescence is yet to be fully developed despite its importance in biolabelling. In particular, bipyramidal gold nanorods have received a large amount of interest as a biolabelling due to highly localised field at their tips, which provide enhancement for emission processes. However, no proper evaluation of geometrical properties of bipyramids such as tip shape, curvature, pentagonal cross section or the waist have been conducted on the field enhancement and peak evolution. Numerical simulations using finite element analysis show that small change in tip radius of curvature can change nonlinear process such as two-photon luminescence (TPL) two to four-fold increase. However, such large increase is not observed in experimental measurement of TPL with respect to tip curvature, indicating that there is fundamental limit to how the field enhancement can influence emission processes.

Here we present a simple analytical theory based on quasistatic field around prolate spheroids to account for bipyramidal shape with correction factors to approximate the shape difference [1]. In doing so, we also present the modified theory for hemispherically-capped cylindrical nanorods, which are more common structure for nanorods. Quasistatic theory for a prolate spheroid has been used to approximate various rod structures, but such approximation can lead to orders of magnitude difference in cross sections, as well as surface plasmon resonance spectra. Prescott et al [2] have previously tried to correct the shape difference from prolate spheroids to the capped cylinders, but this was limited to far-field spectral position, without any detailed analysis on the peak shape, amplitude or near-field enhancements. Accurate correction is highly desirable for correct laser excitation of these rods.

We solved explicit expressions for electric field around prolate spheroids and the derived equations that are compared to the results from numerical methods (Finite element method) for prolate spheroids (Fig. 1). We then extended this theory with the damping factor added to compensate the shape and volume differences for a given aspect ratio. This was used for bipyramids and hemispherically capped shapes of multiple sizes and aspect ratios. For bipyramids, the geometric correction factor incorporates the sharpness of the tip curvature, the volume difference between spheroid to the bipyramid with the same length and width as well as a radiative damping correction. The results are compared with finite element simulations as well as experimental measurement of its action cross-sections. This work will provide an easily accessible and less computational taxing method of predicting plasmonic bipyramid field enhancement and far-field response for future bio-labelling.

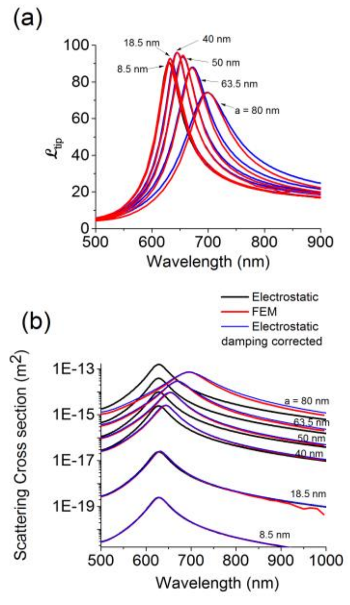

Fig. 1 (a) Field enhancement factor at the tip L_{tip} for an aspect ratio 3.5 gold rod (prolate spheroid) calculated with quasistatic model with respect to wavelength is shown as black line. Together shown are the numerically simulated electrodynamic field enhancement using FEM technique at different gold rod sizes (red lines), and damping corrected electrostatic model (blue lines). Half length of the rod a = 8.5, 18.5, 40, 50, 63.5, 80 nm are specified. (b) Far-field scattering cross sections are shown for the same rods as (a) using the electrostatic (black) and FEM model (red) and damping corrected electrostatic (blue) are shown.

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References

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