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Modeling and Applications of IR Metamaterials Sample Uniform Reproducible SERS: A New Paradigm

Summary

The process of electromagnetic field enhancement in the vicinity of one or more metallic nano-particles (MNPs) can be viewed as a two step process: First, the excitation of a localized surface plasmon resonance (LSPR) resulting from a Mie scattering event of the incoming probe beam [1-4]. Second, localized dipole moment oscillations instigated by the LSPR charge oscillations give rise to MNP-specific radiation patterns that are now acting as coupled nano-antenna arrays. Additional enhancement over the single MNP case maybe achieved by overlapping the LSPR of several neighboring particles. In this case special attention must be paid to ensure that all the participating particle possess the same orientation relative to the probe beam polarization to ensure the overlap of their LSPR modes. Because of the distances involved and the rapid spatial decay of the MNP-LSPR this essentially limits us to dimer effects.

A quick survey of the literature however, shows that the SERS field enhancement factors (EFs) of single MNP-antennas ranges from:10^6-10^7; but for a MNP particle size ranging from 20nm-100nm the surface area packing factor is at the most 10^{-3}. This means that we are 7 orders of magnitude away from the ultimate goal of an average enhancement single molecule sensitivity requiring an factor of 10^{14}. And though one can design particle to give single MNP-EF of 10^8 and dimmers of 10^{10} but these are impractical and cannot be fabricated. Even under the false pretence assuming that we could get there by MNP design the inevitable fact is that the particles would have to be impractically sharp and the fabrication errors will mandate a rounded corner thereby implying that the EFs will never reach 10^{14}.

Further more despite the consensuses that dimers yield higher "hot-spot" EFs, and aside from the occasional irreproducible literature EF of as high as 10^{14} that resulted from random conglomeration of particles, readily reproducible numbers only as high as 10^8 have been reported. The issue here is that the fields die off depending on the particle shape almost exponentially (e^{-r}) or as inverse of the cubic distance away from the surface ($1/r^{-3}$), and since one cannot reliably and reproducibly place particles that are 20nm in size, in an array configuration, closer than 3nm-5nm this implies that reproducible gain orders of magnitude are limited to about 10^2. However "real-estate" wise, one only gets 25% of the spots dimer-pairs case and 50% in the linear array case; thus resulting in an aerial-packing factor density loss of 1order of magnitude (10^{-1}). Hence the overall practical dimer gain in a 2D arrangement is capped at 1 order of magnitude (10^1).

The approach of relying only on MNP design is further complicated by the fact

that, practically, no 2 particles will be identical this is mainly due to fabrication errors. Thus the viability of a MNP choice/design will depend on the interplay between the spectral bandwidth of the LSPR, the spatial extend and overlap of the excited/selected MNP-antenna radiation pattern or mode, and the mode overlap of two similar but non-identical particles. More over, since reproducible dimmer separations can not be made arbitrarily small, it is imperative to realize that one may have to sacrifice the operation in the mode displaying highest field enhancement in exchange for a longer spatial extent of the radiation mode.

Another alternate to higher EFs is to increase the density of the "hot spots" is by deviating from spherical particles while maintaining a relatively smooth edge. Such spheroids allow for the dialing of different oscillation modes: dipoles, quadrupoles, hexapoles , etc. that not only increase the number of hot spots, but also posses-soscillation modes that have characteristically long spatial extent beyond the particles surface or in some case that cove more than 50% of the MNP surface, Figure 2. This dialing in of select MNP-antenna modes can either be done either by tuning the pump frequency and/or controlling the aspect ratio of the MNP-antenna. *Thereby we are led to the conclusion that we need a new paradigm to compensate for the Areal-pacing factor.*

References

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