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Plasmonic enhancement of spontaneous emission and scattering of light in nanostructures

S. V. GAPONENKO
Stepanov Institute of Physics, NASB, Minsk 220072 Belarus

Mechanisms and experimental performance of photoluminescence and Raman scattering enhancement are considered in the context of their application in novel luminophores and high sensitive spectral analysis. So-called "hot spots" are treated as local areas in plasmonic nanostructures where high Q-factors develop both for incident light frequency and for emitted or scattered light frequency. Feasibility of 10- to 10^2-fold enhancement is highlighted for luminescence. Rationale is provided for 10^{14} enhancement factor for Raman scattering which has been claimed based on experimental observation but to date has never been reported in the theory.

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1. Introduction

Nanostructures with characteristic surface relief of the order of 10…100 nm are known to modify spatial distribution of incident electromagnetic field. Local field enhancement results in enhanced absorption of photons by molecules or nanocrystals adsorbed at the surface. The effect is extremely pronounced in metal—dielectric structures because of surface plasmon resonance. A systematic application of the field enhancement in Raman scattering enhancement and in photoluminescence enhancement with respect to molecular probes is followed nowadays by application of the effect with respect to nanocrystals (quantum dots) adsorbed at metal-dielectric nanotextured surfaces. It is the purpose of the present paper to outline mechanisms of photoluminescence enhancement and Raman scattering enhancement and factors in the context of their application in novel luminophores and high sensitive spectral analysis. We consider not only the local field enhancement in terms of excitation process but also photon density of states enhancement effect on photon emission processes with Raman scattering as a specific case of photon emission. In this consideration, scattering of light experiences enhancement as spontaneous emission does. Differences in scattering and luminescence enhancement are due to quenching processes which are crucial for luminescence and less pronounced for scattering. We consider ultimate experiments on single molecule detection by means of enhanced Raman scattering and photoluminescence enhancement of atoms, molecules and quantum dots and the approaches to efficient substrates fabrication for the purposes of ultrasensitive spectroscopy.

2. How secondary emission can be enhanced?

The secondary radiation coming out from a quantum system interacting with incident light can be classified in terms of luminescence, inelastic (Raman) scattering and elastic (Rayleigh) scattering. All types of secondary radiation can be enhanced by means of concentration of incident field and local density of photon state at the site where an emitter is placed.

In terms of quantum electrodynamics, spontaneous emission of photons by a really excited quantum system and spontaneous scattering of photons by a virtually excited system are considered alike in a sense that the number of emitted/scattered photons $I_0(\omega')$ into a mode with frequency ω' per unit time for both type of processes is directly proportional to the incident photon flux $I_0(\omega)$ with ω being the frequency of incident electromagnetic radiation, and density of photon states $D(\omega')$. In other words, one can write an expression,

$$I_0(\omega') = I_0(\omega)[\text{Interaction Term}]D(\omega'). \qquad (1)$$

Interaction term is to be explicitly calculated for every specific process taking into account interaction cross-section, quantum yield (for spontaneous emission) for a given quantum system and quantum process under consideration. In a specific case of resonant (Rayleigh) scattering one has always $\omega=\omega'$.

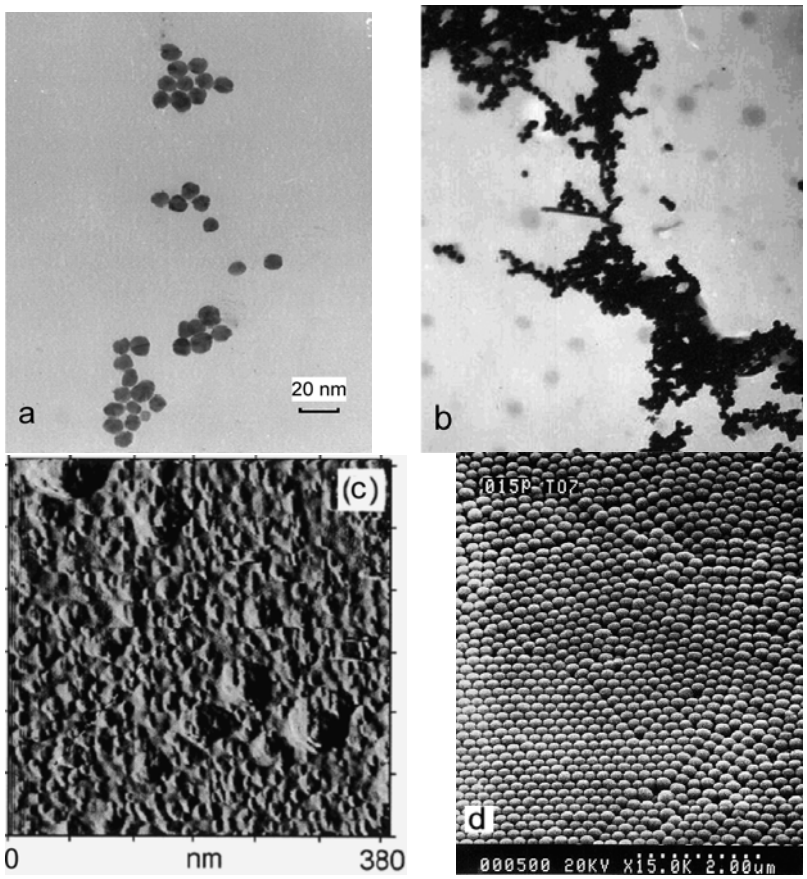

Fig. 1. Representative metal-dielectric structures exhibiting enhancement of Raman scattering and photoluminescence. (a) Gold colloidal particles in a solution, mean diameter is about 10 nm; (b) Fractal-like silver clusters on dielectric surface, particle mean diameter is 15 nm; (c) gold deposited on an irregular nanotextured surface, image size is 380 nm x 380 nm; (d) gold deposited on a regular nanotextured surface formed by close-packed silica dielectric globules, globule diameter is about 200 nm.

The role of photon density of states (DOS) in spontaneous emission of photons is well established and recognized [1, 2]. Since the pioneering paper by E. Purcell in 1946 [3] predicting modification of spontaneous decay rates for radiofrequencies and first experiments in the optical range by K. H. Drexhage in 1970[4], modification of spontaneous decay rate because of spectral/spatial redistribution of photon density of states have been demonstrated for a number of mesoscopic structures with molecules, ions, and quantum dots used as elementary probe quantum systems. A non-exhaustive list includes microcavities [5], photonic crystals [6], heterostructures and interfaces [7], dielectric slabs [8]. However photon density of states effects on spontaneous scattering of light in mesoscopic structures has been involved into consideration only recently [9 -11]. Introduction of photon DOS effects into consideration of giant Raman signals in surface enhanced spectroscopy should noticeably contribute to the value of experimentally observed enhancement factors. It is reasonable to note one essential physical difference of elastic (Rayleigh) scattering of photons as compared to spontaneous photon emission and inelastic (Raman) scattering. Spontaneous emission and inelastic scattering result in photons with different frequency as compared to the incident radiation. For this reason elementary acts of photon emission/scattering can be understood only within the framework of quantum electrodynamics. Elastic scattering results in modification of direction and polarization of incident light and most probably can be completely understood in terms of classical wave theory as a result of multiple scattering and interference of scattered waves. Therefore the photon DOS concept is not necessary to describe elastic scattering in complex nanostructures. However certain intuition promoted by the DOS concept can be helpful in many complex structures for which correct calculation of multiple light scattering is difficult but tentative redistribution photon DOS is qualitatively understood.

3. Rationale for ultimate enhancement factors in Surface Enhanced Raman Scattering

To advance a rationale for single molecule detection by means of SERS reported by several groups [12], the combined effects of the incident field enhancement factor

and DOS enhancement promoted by surface plasmon resonance near a metal nanobody has been accounted consistently [10]. Raman scattering cross-sections have been calculated for a hypothetical molecule with polarizability 10^3 Å^3 placed in a close vicinity near a silver prolate spheroid with length 80 nm and diameter 50 nm and near a silver spherical particle with the same volume. Polarization of incident light has been chozen so as the electric field vector is parallel to the axis connecting a molecule and the center of the silver particle. Maximal enhancement has been found to occur for molecule dipole moment oriented along electric field vector of incident light. The position of maximal values of Raman cross-section is approximately by position of maximal absolute value of nanoparticle's polarizability. For selected silver nanoparticles it corresponds to 383.5 nm and 347.8 nm for spheroid, and 354.9 nm for sphere. To account for local incident field enhancement factor the approach described by M. Stokmann in Ref. [12] has been applied. To account for local density of states enhancement factor, the approach used for calculation of radiative decay rate of an excited atom near a metal body [13] was used. We adopt the approach defining local density of states as a measure for radiative decay rate of a probe quantum system at the point in question. The results are presented in Fig. 2.

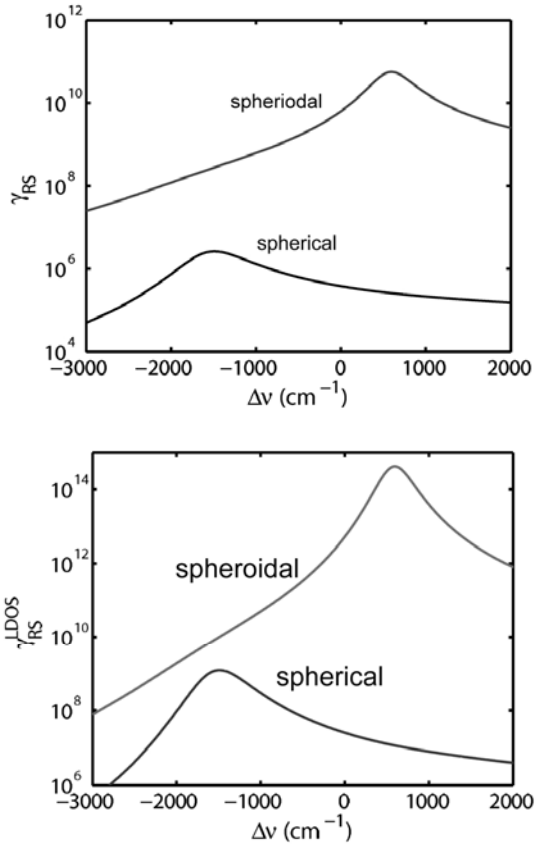

Fig. 2. Calculated Raman scattering cross-section enhancement factor versus spectral shift due to (top) local incident field enhancement without and (bottom) with local density of states effect.

One can see the combined effects of plasmonic enhancement of incident field and photon DOS for output frequency do provide a reasonable rationale for the extreme Raman signal enhancement observed in single molecule experiment. Further progress is espected to come from more advanced models including coupled spheres and ellipsoids as well as more complex metal nanostructures.

4. What is “a hot spot”?

Based on the above consideration, we arrive to the notion of the so-called “hot spots” in plasmonic nanostructures. These are such places on a nanotextured metal surface or near metal nanobodies where simultaneous spatial redistribution of electromagnetic field occurs both at the frequency of the incident radiation ω and at the frequency of scattered radiation ω'. The first effect is the so-called “the field enhancement factor” whereas the second is local density of states enhancement.

A simple treatise in terms of energy conservation lead to a conclusion that incident field enhancement can be readily understood in terms of high Q-factor for incident light. Notably, enhancement of secondary radiation occurs within the framework of the linear light—matter interaction which is unambiguously implied by the linear input—output relation. Therefore, local field enhancement for incident light can not be interpreted as surface redistribution of incident light, i.e. as a kind of local light “microfocusing” as commonly anticipated by many authors. Within the framework of linear light–matter interaction (contrary to e.g. surface enhanced second harmonic generation) the total signal harvesting from a piece of area containing statistically large number of molecules will be same independently of surface redistribution of light intensity. Then strong enhancement for secondary radiation by means of incident field enhancement can only be understood in terms of high local Q-factors for incident light, i.e. in terms of light *accumulation near the surface* rather than light *redistribution over the surface*. Q-fold rise up of light intensity then occurs near hot points as it happens in microcavities and Fabry—Perot interferometers. However, accumulation of light energy needs certain time. Therefore huge signals can develop only after certain time which is necessary for transient processes to finish resulting in steady increase of incident light intensity near hot points as compared to average light intensity in incoming light flux. Transient experiments are therefore to be performed to clarify Q-factor effects in hot points formation.

Enhancement of photon local density of states starting from the pioneering paper by E. Purcell [3] can be interpreted as development of the certain Q-factor in the space region where a test emitter (atom or other quantum system) is placed. Since Q-factor implies a possibility of the system to accumulate energy (the Q value equals the ratio of energy accumulated in the system to the portion of energy the system looses in a single oscillation period), formation of high local density of states areas in many

instances can be treated as development of multiple microcavities at the frequency ω' over a nanotextured metal surface. Experimentally, mapping of surface distribution of high LDOS areas can be performed by means of scanning near-field microscopy. Therefore, "hot spots" are local areas in plasmonic nanostructures where high Q-factors develop both for incident light frequency and for emitted (or scattered) light frequency.

Simple nanostructures exhibiting plasmonic enhancement of spontaneous emission and Raman scattering of light are isolated and aggregated nanoparticles. Further examples of plasmonic nanostructures are nanotextured thin film of metal on a dielectric substrate fabricated by means of vacuum deposition and annealing as well as regular nanostructure developed by means of metal deposition in vacuum on top of close-packed silica balls or a template defined by means of electron beam lithography. Noble metals like Ag, Au, Pt and Ni are used. Though other metals can also be exploited, their strong oxidation in air prevents desirable proximity of a probe to metal surface.

"Hot spots" promise enormous enhancement of the secondary radiation emitted by molecules or other species located in the proper positions within plasmonic nanostructures. When multiplying incident field enhancement and LDOS enhancement, e.g. for a spheroidal metal particle, one can get the product of the order of 10^{10}. Such values can never be obtained for photoluminescence enhancement (because of the competitive non-radiative bypass) but these can even be exceeded in surface enhanced Raman experiments. Experimental performance for plasmonically enhanced luminescence are reported for different kind of luminophores, namely, lanthanide ions, organic molecules, and semiconductor nanocrystals (quantum dots) [14-17]. Feasibility of 10-fold enhancement is highlighted whereas higher values are possible for regular metal structures fabricated by electron beam lithography with the overall enhancement factor not exceeding 10^2.

5. Conclusion

The brief overview of mechanism for plasmonic enhancement of scattering and spontaneous emission of light in terms of incident field enhancement and local density of states enhancement near metal nanobodies provides a promising prospective for its purposeful applications in the extreme molecular analysis and light-emitting components for display applications.

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*Corresponding author: s.gaponenko@ifanbel.bas-net.by