

Surface Plasmon-Enhanced Spectroscopy and Photochemistry

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Received: 18 April 2007 / Accepted: 16 July 2007 / Published online: 17 August 2007
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Abstract A review of selected recent contributions to the area plasmon-enhanced spectroscopy and photochemistry is presented.

Keywords Surface plasmons · Surface-enhanced Raman spectroscopy · Surface-enhanced infrared absorption · Surface-enhanced fluorescence · Extraordinary optical transmission · Photochemistry

Introduction

Surface plasmons (SPs) are collective electronic excitations near the surfaces of metallic structures [1, 2]. SPs can generally be described well with continuum classical electrodynamics and correspond to evanescent wave solutions of Maxwell's equations when appropriate material properties and boundary conditions are considered. Both non-propagating or localized SPs (LSPs), and propagating or SP polaritons (SPPs) are possible. The absorption or extinction spectra of metal nanoparticles exhibit LSP resonances, typically in the visible-UV range [3], although with appropriate design, e.g., the use of core/shell particles, resonances in the near-infrared and infrared are possible [4]. In contrast, as long as the real part of the dielectric constant is negative, a necessary material condition for plasmons, SPPs on metal films can be excited with light in a wide range of wavelengths using, for example, attenuated total reflection techniques [2]. The

evanescence, or confinement, of the field near the metal surface allows for the possibility of near-field intensities that are significantly enhanced compared to the incident radiation. This is particularly true for LSP excitations on metal nanoparticles or nanostructured (rough) metal films and related metallic nanostructures.

If E_0 denotes an incident plane wave, let the local field in the vicinity of a metal surface be written as $E_L = g E_0$. If the incident light has wavelength close to an LSP resonance, then the amplitude enhancement factor, g , can be considerably greater than unity in certain regions of the nanoparticle. While there is much variation in estimates of g depending on specific details of a given problem and the level of theory being used, realistic amplitude enhancements have been estimated to be on the order of 10 – $10^{2.5}$ [3].

Molecular responses arise from the interaction term, $-\mu \cdot E_L$, in the Hamiltonian describing matter–light interactions, where μ is the molecular dipole with the non-static or dynamic contribution being most relevant. Thus, if a molecule is close to a metallic nanostructure being illuminated with light near an SP resonance, an enhanced molecular spectroscopic response is expected due to the increased importance of this interaction term. If a spectroscopic response is proportionate to the absolute square of a matrix element involving this term, as is typical for a one-photon allowed molecular transition, an enhancement of g^2 would then result. This is the situation for surface-enhanced infrared absorption (SEIRA) [5], for example. However, if two or more photons are involved in the process, the enhancements can be significantly higher. The most well-known surface plasmon-enhanced spectroscopy is surface-enhanced Raman spectroscopy (SERS) [6], which can exhibit enhancements on the order of g^4 [7, 8], i.e., 10^4 – 10^8 . This factor can be thought of as arising from a product of

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enhancement factors for absorption and emission. Actually, in addition to the electromagnetic (EM) enhancement being discussed in this paper, there is a chemical enhancement due to molecule–metal electronic interactions modifying the molecular level structure and transition moments. The chemical effect is now believed to be generally smaller than the EM effect but can still contribute up to an additional order of 10^2 to the overall enhancement [9]. Surface-enhanced fluorescence (SEF) [10, 11] is another example of a plasmon-enhanced spectroscopic process. The final plasmon-enhanced spectroscopy of interest here is what has been termed extraordinary optical transmission (EOT), which involves enhanced transmission of light through metal nanostructures [12]. It is also natural to expect that certain photochemical reactions could be enhanced in appropriate metallic nanostructures [13, 14].

I review here selected papers on plasmon-enhanced spectroscopy and photochemistry. This is not an exhaustive review, but rather one designed to provide an introduction to the general area and a few inroads into the current literature.

Spectroscopy

The four different types of plasmon-assisted spectroscopies noted in the introduction, SEIRA, SERS, SEF, and EOT are discussed.

Surface-enhanced infrared absorption

I discuss SEIRA first because it is conceptually the simplest surface-enhanced spectroscopy. SEIRA has now been actively studied for over 25 years [5]. A 2001 review of the area is a good introduction [15].

As noted in the Introduction, the nature of the SEIRA process is such that enhancements are on the order of g^2 , where g is the LSP enhancement factor noted in the Introduction. It should also be noted that SEIRA is often carried out on metal films composed of metal islands and that at IR wavelengths, one may be accessing the tail of a broad LSP resonance centered on lower wavelengths. Compared to SERS, there is therefore a small enhancement, typically in the 10–100 range, which is why the amount of SERS work dwarfs the work on SEIRA. Nonetheless, the area remains reasonably active, particularly due to advances in nanoscience and nanotechnology. Some interesting recent SEIRA work includes the SEIRA of C_{60} [16], a demonstration that SEIRA on ultra-thin metal films can be a sensitive analytic tool [17] and a theoretical simulation combining rigorous electrodynamics with quantum mechanics of a model for enhanced infrared multiphoton absorption [18]. Infrared spectroscopy is, of course, an

extremely important and complementary tool to Raman spectroscopy. From a practical perspective, it is likely that a combination of the SERS and SEIRA will provide the greatest analytical capabilities [19, 20].

Surface-enhanced Raman spectroscopy

SERS is the oldest and by far the most successful of all the spectroscopies utilizing near-field enhancements due to surface plasmon excitations [6]. There are many excellent reviews of SERS, including [8, 21, 22]. A recent *Faraday Discussion* on SERS is reflective of the breadth of modern SERS research. See, e.g., the introductory lecture [23] and concluding remarks [24].

As [23, 24] attest, a great deal of this modern research is making use of nanotechnology, in particular, top down fabrication techniques that allow for tailored and reproducible SERS responses and sensing capabilities. In addition, particularly exciting has been the fact that the huge enhancement factors have allowed the spectroscopic response of just one molecule to be explored [25–27]. In terms of the theory behind SERS, theoretical studies are now emerging that treat, with rigorous electronic structure theory methods, molecules interacting with (small) metal clusters [28]. This work, and extensions thereof, should considerably clarify the relative roles of electromagnetic and chemical enhancements.

Surface-enhanced fluorescence

The modification of molecular fluorescence (or more generally luminescence) due to plasmon excitations has a long history that includes important early experimental [10, 11] and theoretical [29, 30] contributions. SEF is in some ways more subtle than SERS, despite it being also a two-photon process. For example, it is quenched if the molecule is too close to the metal where the EM enhancement factors, g , are greatest. Furthermore, while like SERS the fluorescence enhancement factor [30] involves a product of enhancement factors for absorption and emission, the radiationless transitions before emission of the second photon in fluorescence result in a broader range of emission frequencies. As a consequence, SEF enhancements are less than the SERS g^4 factor, and are more on the order of g^2 as in SEIRA. Nonetheless, owing to the immense importance of fluorescence in biology and biochemistry and advances in nanotechnology, SEF and related plasmonic/fluorescence phenomena such as surface plasmon-coupled emission are very active research areas, as is apparent from two recent review articles [31, 32].

Some recent advances in SEF include, for example, the use of nanotechnology fabrication techniques to obtain highly reproducible SEF responses from CdSe/ZnS collo-

dal nanocrystals [33], the demonstration of significant SEF from dyes by optimizing nanoparticles for higher scattering efficiency [34], and a demonstration that plasmons can radiate a fluorophore's structured emission [35].

Extraordinary optical transmission

In EOT, actual molecular transitions are not necessarily relevant. Rather, when light is passed through some metallic nanostructure such as a metal film with subwavelength size holes, the spectrum of transmitted light exhibits complex spectral features related to LSP and SPP resonances. The sensitivity of these features, i.e., the variation of peak intensities and positions with the nature of any substrate makes these systems potential chemical and biological sensors. Much of the work in this area was motivated by the first demonstration of EOT in 1998 [12].

The nature of EOT spectra has often been debated in the literature, as different phenomena can occur at different wavelengths and a single, simple explanation of all spectral features is generally not possible. Nonetheless, recent work has established the clarified the role of SPs [36, 37].

In other recent work arrays of silver nanowells formed by electron beam, evaporation of gold onto polymer masks were shown to be highly sensitive to small refractive index changes in a substrate, making them good candidates for possible sensors [38]. An important feature of this work was the use of rigorous computational electrodynamics methods to explain this sensitivity and identify the nature of the most important spectral peaks.

Of course the light scattering by arrays of nanoparticles, as opposed to nanoholes, can also be used in a similar sensing capacity and has some advantages as recently noted in [39].

Photochemistry

The previously discussed spectroscopic processes did not involve chemical change. The possibility of plasmon-enhanced photochemistry was suggested in theoretical work in 1981 [40, 41]. Subsequent experimental verification came 2 years later in the demonstration of enhanced UV photodissociation of organometallic molecules adsorbed on a rough metal surface [13]. See also work in [14]. Despite these early developments, this area is still relatively unexplored.

One interesting recent example plasmon-enhanced photochemistry is the synthesis of silver nanodisks via plasmon-enhanced photoreduction of adsorbed silver ions [42]. A remarkable feature of these experiments is that the shape of the resulting nanoparticles could be controlled by altering the irradiation wavelength. This is made possible

because of the shape dependence of the surface plasmon absorption.

Another recent development in plasmon-enhanced photochemistry is the use of surface plasmon excitations to induce *trans-cis* isomerizations in azodye molecules doped in polymers that are deposited over nanoparticles [43]. The SP resonance of the gold nanoparticles in this study overlapped with the azodye absorption consistent with *trans-cis* isomerization. The repeated molecular isomerizations that occurred during illumination of the sample resulted in movement of the polymer material that the azodyes were embedded in away from the plasmon hotspots (the general problem of the nature of the material response given the presence of optically induced azodye isomerizations is still an interesting and open area for exploration [44]). Subsequent atomic force microscopy measurements then allowed a mapping of the "negative image" of the underlying plasmon fields, i.e., essentially a new means of imaging SP near-fields.

Concluding remarks

In this brief review of selected contributions to the general area of surface plasmon-enhanced spectroscopy and photochemistry, I hope to have convinced the reader that this is an exciting, evolving scientific area. Particularly with the continued, rapid advances in nanofabrication and nanotechnology, many new fundamental and practical developments are anticipated.

Acknowledgments This work was supported by the US Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences under contract DE-AC02-06CH11357.

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