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Viewpoint

A fluctuating fractal nanoworld

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Observations in nanostructured gold films, impossible until now, confirm theoretical predictions about how optical energy is localized in strongly scattering disordered materials.

Subject Areas: **Optics, Nanophysics**

A Viewpoint on:
Fluctuations of the Local Density of States Probe Localized Surface Plasmons on Disordered Metal Films
V. Krachmalnicoff, E. Castanié, Y. De Wilde and R. Carminati
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The localization of elementary excitations in complex media is one of the most universal and important problems of physics, spanning the range from electrons in disordered materials to acoustic waves in nonuniform media, to light waves in the presence of random scatterers. One of the most fundamental effects in this wide class of phenomena is Anderson localization [1]. This effect is predicted for both classical waves and quantum-mechanical states in random scattering media and is deeply rooted in general properties of time reversal, which dictate that back-scattered waves add coherently to the original wave packet, leading to its localization. For electrons, the properties of this localization are influenced by, and can be obscured by, electron-electron interactions. In contrast, in linear optics, the propagation and scattering phenomena involve noninteracting photons (or electromagnetic waves in the classical picture). In this case, the scattering can lead to Anderson localization in its purest forms. One of the practical implications of the light localization in strongly scattering media is, for instance, random lasers [2]. Now, as reported in *Physical Review Letters*, Valentina Krachmalnicoff, Etienne Castanié, Yannick De Wilde, and Rémi Carminati of the Institut Langevin in Paris [3] have, for the first time, experimentally observed the near-field localization and fluctuations of optical energy on a multitude of length scales in disordered nanoplasmonic metal systems.

In general, electromagnetic waves in a dielectric cannot be localized to less than half their wavelength in that medium because this is the distance needed to exchange energy between the electric and magnetic components of the electromagnetic field. However, in plasmonic metal systems this limitation is completely relaxed because the optical energy is carried by surface plasmons, which, in contrast to quanta of electromagnetic waves (photons), are electromechanical oscillations and are not restricted by a characteristic wavelength. Therefore, the optical energy can be localized at a minimum scale, limited only by the finest inhomogeneities of the metal down to a few nanometers, where Landau damping in the metal's electron plasma sets the lowest scale, $v_F/\omega \sim 1$ nm, where v_F is the electron velocity at the Fermi surface (typically $\sim 10^6$ m/s), and ω is the light frequency. A universal phenomenon in the localization of optical energy in strongly inhomogeneous plasmonic media is the formation of hot spots, which my colleagues and I considered earlier [4, 5]. This phenomenon is illustrated in Fig. 1(a), which shows a calculated distribution of the local electric field for a fractal cluster (modeled as a cluster-cluster aggregate) under excitation by a plane wave. The cluster responds with a highly nonuniform, spatially fluctuating field with spikes (hot spots) in nanometer-size regions determined by the minimum scale of the nanoplasmonic system.

Our initial assumption was that for strongly inhomogeneous plasmonic systems, such as a fractal aggregate of plasmonic metal nanoparticles, whose geometry is illustrated in the inset of Fig. 1(a), there is strong Anderson localization where the fields of a plasmonic eigenmode decay exponentially away from the hot spot [5]. This hypothesis was developed in a number of theoretical publications and some initial experiments (see Ref. [6] and references therein).

However, our further theoretical work predicted a very different picture of plasmonic nanolocalization of the optical energy for the disordered clusters of plasmonic metal nanoparticles, which we called inhomogeneous localization [7, 8]. In this picture, there are different plasmonic eigenmodes, which coexist at close frequencies and have completely different localization sizes, ranging from the minimum scale (down to a few nanometers) to the scale of the entire systems. Each eigenmode may consist of a different number of sharp hot spots. These hot spots and their localization radii

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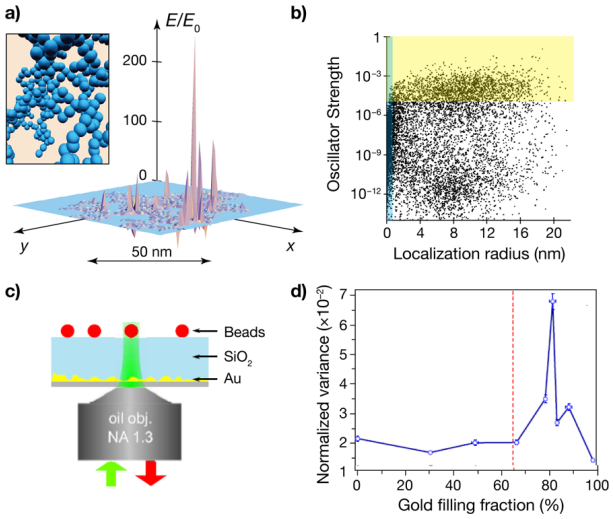

FIG. 1: Inhomogeneous localization of nanoplasmonic eigenmodes. (a) Calculated local optical fields inside a fractal nanocluster made of silver nanospheres. Insert: geometry of such a cluster. (b) Surface plasmon eigenmodes for a semicontinuous metal nanofilm plotted against their oscillator strength and localization radius. The yellow background marks the bright (luminous) eigenmodes, the blue background highlights the strongly localized eigenmodes. (Adapted from Ref. [10]). (c) Schematic of experimental observation of the surface plasmon local fields. (From Ref. [3]). (d) Measured normalized variance of the decay rates of the dye molecule fluorescence. (From Ref. [3]). The red dashed vertical line qualitatively shows the onset of the significant fractality of the underlying metal clusters.

fluctuate strongly with the optical frequency and from cluster to cluster. Each such eigenmode is reminiscent of the local field distribution shown in Fig. 1(a). This inhomogeneous localization is the underlying reason for the giant fluctuations of the local optical fields in disordered plasmonic nanoclusters [9].

The properties of inhomogeneous localization and its dramatic difference from strong localization are demonstrated in Fig. 1(b) [10]. For a fairly large cluster containing more than 10^3 constituent nanoparticles, each plasmonic eigenmode is shown as a point in coordinates of oscillator strength f_n and localization radius L_n. This localization radius is calculated as a root mean square radius of the local eigenmode field $E_n(r)$. The oscillator strength determines the absorption cross section of the system. As one can see, there are eigenmodes of all localization radii and oscillator strengths present in this cluster. We have also found out that this property is almost uniform across all frequencies: such coexistence of the eigenmodes takes place at each frequency within their range of existence.

As normalized in these calculations, the dipole sum rule is $\Sigma f_n = 1$. Thus one can expect that a typical bright eigenmode (out of $\sim 10^4$ eigenmodes of the system) will have an oscillator strength $f_n \sim 10^{-4}$. Such eigenmodes are highlighted by the yellow background in Fig. 1(b). The maximum localization length for our system is $L_n \sim 25$ nm and the minimum length is $L_n \sim 1$ nm. The blue background in Fig. 1(b) highlights the strongly localized eigenmodes with $L_n \sim 1$ nm. We see that practically all strongly localized eigenmodes are dark. This is not accidental and is actually a rigorously proven property [10]. This means that there is strong Anderson localization for a fraction of the eigenmodes, but these eigenmodes and many other dark eigenmodes of the system (outside of the yellow highlighted area) cannot be excited or observed from the far field. In fact, only a minority of the plasmonic eigenmodes are bright. This presents a formidable experimental challenge.

Full information on the inhomogeneously localized eigenmodes of the system can only be obtained using near-field excitation and observation. However, using near-field probe microscopy as in Ref. [11] is not advisable because the metal nanotip in such microscopes is a strongly perturbing object that can distort the fine features of the localization. One possible approach to this problem is electron-loss spectroscopy [12]. However, this method does not provide direct information on the strength of the local plasmonic eigenmode fields and also has only been applied thus far to the simplest geometries, but not to large disordered nanoplasmonic clusters of interest.

Krachmalnicoff *et al.*[3] employ an original and fundamentally different method, illustrated in Fig. 1(c). Their probe is a dielectric nanobead containing fluorescent molecules. They deposit such beads randomly at the surface of the dielectric nanofilm covering the nanostructured system. These nanobeads are in the near field (at a distance of a few tens of nanometers) of the metal plasmonic nanostructure under investigation—a gold semicontinuous nanofilm consisting of a random planar composite of gold nanoparticles that can have a desired fill factor of the metal (in the plane of the structure) from 0 to 1. These nanobeads are in a low concentration, so the distances between them are large, and they are independently addressable with a far-field optical microscope. They are excited by optical pulses, and their decay rates, Γ, are measured with time resolution. Note that, theoretically, the decay rate of a chromophore in the vicinity of a metal nanostructure is proportional to the local density of its plasmonic eigenstates, which, in turn, is proportional to the intensity of the local fields, $E^2(r)$, where r is the position of the fluorescent probe, and $E(r)$ is the local field.

With this method of measuring the distribution of the decay rates, one actually gets direct access to the distribution of the local field intensity. The quantity measured in Ref. [3] is the normalized variance (NV) of decay rates,

$$\mathrm{NV} = \frac{\sigma^2(\Gamma)}{\langle\Gamma\rangle^2} = \frac{\langle\Gamma^2\rangle}{\langle\Gamma\rangle^2} - 1 \approx \frac{\langle E^4(r)\rangle}{\langle E^2(r)\rangle^2} - 1, \qquad (1)$$

and it is reasonable to assume, as is done by Krach-

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malnicoff *et al.*[3], that the field under each individual nanobead is dominated by a single eigenmode. In that case, the measured variance is just $V/V_L - 1$, where V is the total volume of the nanostructure and V_L is the volume in which an eigenmode is localized. Thus this normalized variance is a direct measure of the eigenmode localization, which includes both the bright and dark eigenmodes.

The results of these measurements are shown in Fig. 1(d). One can see that for the fill factor below $\sim$ 60%, the NV stays low and constant, which implies low local density of optical states and weakly fluctuating local fields. In sharp contrast, for higher fill factors, the NV increases sharply, by a factor ~ 3, which shows that there are hot spots appearing in the near field. These hot spots have modal volumes V_L significantly less than the system's volume V and are responsible for the increase of NV. This is precisely the picture of the inhomogeneous localization.

Almost 15 years after its prediction [7, 8], a convincing observation supporting the inhomogeneous localization of the plasmonic eigenmodes on fractal clusters of gold has been obtained by Krachmalnicoff *et al.*[3]. The onset of the inhomogeneous localization is detected through the enhanced fluctuations of the decay rates of organic dye molecules placed in the near field of the system, which is related to the giant fluctuations of the local optical field intensity. This observation has both fundamental and applied importance. Fundamentally, it experimentally confirms the new phenomenon of the inhomogeneous surface-plasmon localization and the related giant fluctuations of the nanolocalized optical fields in fractal nanostructured metals. These properties determine the highly enhanced nonlinear optical responses and giant surface enhanced Raman scattering (SERS) from such systems. Regarding applications, SERS from random metal surfaces and fractal clusters [13] is used for detection and monitoring of minute amounts of chemical and biological compounds, which makes understanding of its fundamentals very important. Other areas of application, where localization properties of plasmonic eigenmodes are of primary importance, include efficient solar energy conversion, ultrafast computations and communications in the nanoscale circuits, and, potentially, many others.

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About the Author

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Mark I. Stockman received his Ph.D. and D.Sc. degrees from institutes of the Russian Academy of Sciences. Currently he is Professor of Physics at Georgia State University in the US. He also served as a Distinguished Professor at Ecole Normale Supérieure de Cachan, and Ecole Supérieure de Physique and de Chimie Industrielle, both in France, and as a Guest Professor at the University of Stuttgart, at Max-Plank-Institute for Quantum Optics, and at Ludwig Maximilian University, all in Germany. A major direction of his research is theoretical nanoplasmonics, especially the theory of ultrafast and nonlinear nanoscale optical phenomena. He is a co-inventor of the SPASER (nanoplasmonic laser) and an author of 160 major research papers, and has presented many invited and keynote talks at major international conferences. He has taught courses on nanoplasmonics and related topics at major international meetings and scientific institutions in the US, Canada, Europe, Asia, and Australia. In 2008 he was recognized as an Outstanding Referee by the American Physical Society.

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