Collective electronic states in inhomogeneous media at critical and subcritical metal concentrations

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The excitation of collective electronic states, surface plasmons (SPs), is studied for semicontinuous metal films at various metal concentrations. A previously unexpected strong optical response, manifested through an increase in the exponents of the local field moments, is predicted at noncritical metal concentrations. This phenomenon results from an increase in SP localization *away* from the percolation threshold, which is opposite to the general understanding that a decrease in the number of scatters leads to weaker mode localization. Experimental results from near-field optical microscopy are found to be in good agreement with the theory, validating the role of SP localization in the optical response. Possible applications in improving the sensitivity of spectroscopic measurements such as surface-enhanced Raman scattering and harmonic generation are considered.

The nature of the electronic wave functions in random media has been a subject of intense studies for the last 50 years.[1–4] In an ideal crystal lattice the electronic states are described with periodic (Bloch-type) wave functions that permit transport throughout the system. The introduction of lattice defects, or impurities, has been shown to impede the electronic motion manifested through localization of the electronic wave functions in a finite region of space. It is now well established that for infinitely large one-dimensional (1D) and 2D systems, and for an arbitrary amount of disorder, all electronic states are strongly (exponentially) localized.[3,4] In the 3D case a critical level of disorder exists at which an insulator-conductor transition could take place.[4]

Recently, the collective electron response in metallic systems has attracted strong attention due to prospective applications in negative-index materials,[5–7] spectroscopy,[8–10] and nonlinear optics.[11] It has been shown that in random metal-dielectric composites (see Fig. 1), local field intensity enhancement of up to 10^4 could be obtained under illumination with light at optical and near-infrared frequencies.[8–11] The strong local fields result from excitation of high-Q factor surface plasmon (SP) resonances and appear to be localized in small spatial areas due to electromagnetic interactions between the randomly distributed metal particles that constitute the composite. While the optical response of the metal films can be phenomenologically understood, the specific nature of the SP states in such systems is still controversial. Historically, one of the first attempts to study the localization of SPs as a result of surface roughness was based on the diffusion approximation, similar to that used in the transport theory.[12] It was shown that propagating SP polaritons tend to localize parallel to the roughened surface with diffusion coefficient approaching zero, similar to the Anderson case.[1,2] A strong localization of the collective electron excitations was also argued based on mathematical similarities between the Schrödinger Hamiltonian in the quantum case and the governing Kirchhoff Hamiltonian (KH) in the classical quasi-static regime.[11] However, in recent works, the existence of *delocalized* SP states, which are due to short-range correlations in the KH, have been demonstrated at critical metal concentrations: the percolation threshold.[13,14] Despite these progresses, the nature of the SPs at noncritical or near-critical metal concentrations is still unknown. In this paper, we present theoretical and experimental studies of the effect of SP localization on the optical response at noncritical metal concentrations. Interestingly, the results suggest an increased local optical coupling and enhancement at noncritical metal concentrations than at the percolation threshold.

In order to model the local electric response of a random planar system comprised of a large number of metal particles (see Fig. 1), we work in the quasistatic limit where the particles size a (and film thickness) is much smaller than the wavelength of illumination, λ. In this case a local potential $\varphi(\vec{r})$ is introduced satisfying the generalized local current conservation

$$\vec{\nabla} \cdot [\sigma(\vec{r})\vec{\nabla}\varphi(\vec{r})] = \vec{E}_0 \cdot \vec{\nabla}\sigma(\vec{r}), \qquad (1)$$

where $\vec{E}_0$ is the incident electric field normal to the film surface and the spatially dependent complex conductivity $\sigma(\vec{r})$ acquires the value $\sigma_m = -i\omega\varepsilon_m$ for the metal particles and $\sigma_d = -i\omega\varepsilon_d$ for the dielectric host with probabilities p and $1-p$, respectively. To solve the current conservation, Eq. (1), and examine the properties of the excited SP states, we first focus on the underlying SP eigenproblem[11,14]

$$\vec{\nabla} \cdot [\Theta(\vec{x})\vec{\nabla}\Psi_\Lambda(\vec{x})] = \Lambda\Psi_\Lambda(\vec{x}), \qquad (2)$$

where $\vec{x} = \vec{r}/a$, Λ and Ψ_Λ are the SP eigenvalues and eigenvectors, and the topology function $\Theta(\vec{x})$ maps the local geometry and has $+1$ and -1 values at the dielectric and metal sites, respectively. Reduction of Eq. (2) on a square lattice
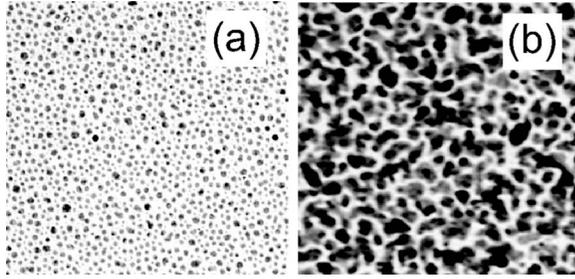
FIG. 1. Random metal-dielectric films synthesized by laser ablation of a solid silver target onto a glass substrate. The metal concentration p is varied by control over the deposition time. At a low concentration $p=0.2$ (a), the sample constitutes of dispersed metal particles with sizes $a=10–20$ nm, while close to the percolation threshold $p=0.65$ (b), large metal clusters span the entire system.

leads to a system of linear equations, where the governing Kirchhoff Hamiltonian is a random matrix with correlated diagonal and off-diagonal elements.[14] The existence of short-range correlations in the SP eigenproblem makes it substantially different from the corresponding quantum mechanical case where the random Hamiltonians are noncorrelated. The correlations in the KH are due to local current conservation and exist for all spatial dimensions. At critical metal concentrations ($p=p_c=0.5$), these correlations result in a singular SP density of states (DOS) $\rho(\Lambda)\sim|\Lambda|^{-\gamma}$ and localization length $\xi(\Lambda)\sim|\Lambda|^{-\alpha}$, with exponents $\alpha\approx\gamma=0.14$. The nature of the singularities in the limit of infinite system sizes is such that the measure of the truly delocalized states asymptotically approaches zero.[14]

Since current conservation holds in all cases, one should expect singular $\rho(\Lambda)$ and $\xi(\Lambda)$ for nonpercolating systems as well. To study this effect we solve Eq. (2), imposing zero-current boundary conditions and vary the metal concentration p. The exact profiles of the generalized density of states $\rho(p,\Lambda)$ and localization length $\xi(p,\Lambda)$ are shown in Fig. 2. With a decrease in p a shift in the DOS is observed toward an increasing number of SP eigenstates that have positive eigenvalues. This phenomenon corresponds to the fact that the eigenproblem maps the underlying film geometry with positive eigenvalues corresponding to eigenstates situated mostly in the dielectric host. Additionally, a strong decrease in the localization length of the SP eigenmodes with negative eigenvalues is clearly visible [see Fig. 2(b)]. This transition is due to a decrease in the size of the metal clusters at lower concentrations p, which affects the maximum size of the SP modes connected with the underlying metal superstructures. It should be pointed out that, while in Fig. 2 we have presented only the results for $p<p_c$, the properties of the SP eigenstates at high metal concentrations $p>p_c$ are equivalent due to symmetry [since Eq. (2) is invariant under the transformation $\Theta\rightarrow-\Theta$ and $\Lambda\rightarrow-\Lambda$]. The invariance of Eq. (2) is only valid in the case of zero loss and means that the system shows similar optical behavior under exchange between the metal and dielectric parts, an effect known in the literature as Babinet's principle. In this case, the relationships $\rho(\Lambda,p_c+\Delta p)=\rho(\Lambda,p_c-\Delta p)$ and $\xi(\Lambda,p_c+\Delta p)=\xi(\Lambda,p_c-\Delta p)$ hold for any given $\Delta p\lesssim p_c$.
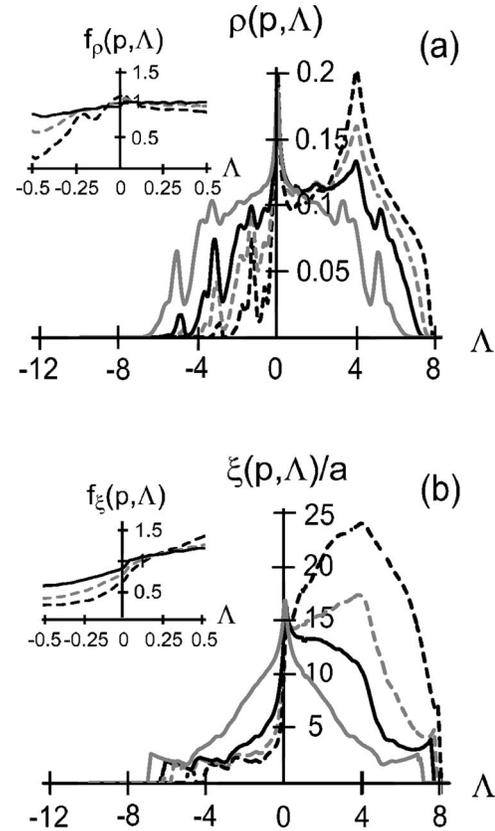
FIG. 2. The surface plasmon density of states (a), and localization length (b), are calculated as a function of the eigenvalue Λ for an ensemble of 100 metal-dielectric films, each with size 1 μm. Four different metal filling fractions are investigated: $p=0.1$ (dashed black line), $p=0.2$ (dashed gray line), $p=0.3$ (black line), and $p=p_c=0.5$ (gray line). The singularity at the band center and its dependence on the metal concentration are closely inspected in the insets.

Using Eq. (2), it is possible to estimate the optical response of the random metal films for an incident frequency ω_r corresponding to the single-particle resonance condition $\mathrm{Re}\,\varepsilon_m(\omega_r)=-\varepsilon_d$ and including the intrinsic metal loss. For that, we expand the local potential $\varphi(\vec{r})$ over the SP eigenspace,[11,14] and obtain an integral relationship for the moments of the local field $\vec{E}(\vec{r})=-\vec{\nabla}\varphi(\vec{r})$ as follows:

$$M_n = \frac{1}{S}\left\langle \int |\vec{E}(\vec{r})|^n/|\vec{E}_0|^n dS \right\rangle$$

$$\approx \int_{-\infty}^{\infty} \frac{\rho(p,\Lambda)[a/\xi(p,\Lambda)]^{2n-2}}{(\kappa^2+\Lambda^2)^{n/2}}d\Lambda, \qquad (3)$$

where $\kappa=\mathrm{Im}\,\varepsilon_m/|\varepsilon_m|$ is the intrinsic loss factor, S is the sample area, and the brackets correspond to ensemble averaging over large numbers of system realizations. For glass-silver composites the intrinsic loss at resonance is small, $\kappa(\omega_R)=0.03\ll1$, where $\hbar\omega_R=3.4$ eV,[15] and only the SP eigenmodes in the vicinity of the band center contribute to the moments. The properties of the generalized SP eigenstates for $|\Lambda|\ll1$ are presented in Fig. 2 as insets. There is a
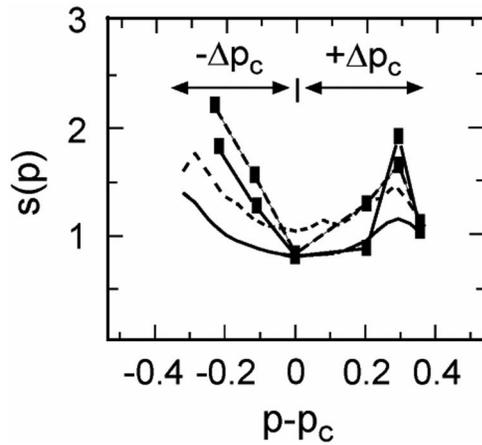
FIG. 3. Slope of local field moments vs metal concentration for numerical (lines) and experimental (connected squares) data. The wavelengths of the incident light are $\lambda = 543$ nm (solid lines) and $\lambda = 633$ nm (dashed lines), respectively.

FIG. 4. Electromagnetic enhancement for surface-enhanced Raman scattering from a silver-glass composite at various metal concentrations. A local minimum is observed at the percolation threshold while maximum enhancement factors of 2×10^6 for $\lambda = 543$ nm (solid line) and 6×10^6 for $\lambda = 633$ nm (dashed line) are obtained at $\Delta p_c = -0.3$ and $\Delta p_c = -0.27$, respectively.

clear shift in the behavior of the eigenmodes for positive and negative eigenvalues. This effect is expected since the band center corresponds to a transition from metallic- to dielectric-based optical modes. Analogous to the metal-dielectric transitions in complex media,[4] the effect of "discontinuity" should become more pronounced with an increase of the system size. Unfortunately, larger system sizes than those considered impose overwhelming computational difficulties. Nevertheless, from the available data and in the first-order approximation, we can write a simplified expression for the normalized SP DOS, $f_\rho(p, \Lambda) = \rho(p, \Lambda) / \rho(p_c, \Lambda) \approx 1$, and the normalized SP localization length, $f_\xi(p, \Lambda) = \xi(p, \Lambda) / \xi(p_c, \Lambda) \approx g(p) + \theta(\Lambda)[1 - g(p)]$, where $\theta(\Lambda)$ is the step function and g is a nontrivial function of p. Using the above expressions, we take out the p dependence in the integral in Eq. (3) and obtain $M_n(p) \approx \frac{1}{2} M_n(p_c)[1 + g^{2-2n}(p)]$, where $M_n(p_c) \approx \kappa^{-(1-2\gamma)n + 1 - 3\gamma}$ are the local field moments at the percolation threshold.[14] Since $g(p) < 1$ for $p \neq p_c$ [$g(p_c) = 1$], we may write $M_n(p) > M_n(p_c) g^{2-2n}(p) > M_n(p_c)$, which implies that for $n > 1$, the local field moments have a minimum at p_c. From Fig. 2(b) it is also clear that for $p < p_c$ the localization lengths of the excited SP eigenstates, predominantly those with $\Lambda < 0$, are lower compared to the critical case ($p = p_c$). Thus, we conclude that at noncritical metal concentrations the role of the localized SP states in the local field statistics becomes stronger. This property of the quasistatic SP resonances is unique and bears no analogy to the wave localization based on wave scattering in random dielectric media.[4]

The increased contribution of the localized states at $p \neq p_c$, or the increase of SP delocalization at p_c, is revealed through the dependence of $\ln M_n$ on the order n. According to the theory, a linear dependence $\ln M_n \sim s(p)n$ is to be expected, with the slope $s(p) = s(p_c) + 2 \ln[1/g(p)] \geq s(p_c) = (1 - 2\gamma)\ln(1/\kappa)$ being higher for metal concentrations away from the percolation threshold. To explicitly study this phenomenon and provide straightforward evidence of the effect of SP localization in the local optical response, we solve Eq. (1) applying an exact numerical procedure,[10] which allows

for calculation of systems with up to 10^6 metal particles. We should point out that, while the system size used in the calculations, 1 μm, is of the order of the incident wavelength, the quasistatic approximation is still applicable since (i) normal illumination is assumed (no phase change along the film surface) and (ii) the characteristic sizes of the resonating metal structures are of the order of the particle sizes (tens of nanometers).[11] In the calculations we also rely on experimental values for the permittivities of silver and for the glass substrate.[15] Our results are presented in Fig. 3 where the theoretical slope $s(p)$ is compared to experimental data obtained by near-field scanning optical microscopy (NSOM) of silver-glass composites (see Fig. 1).

In the experiment, silver-glass composites with metal grain sizes of 20–30 nm and of varying metal concentrations were synthesized by pulsed laser deposition. The morphology of the samples is shown in Fig. 1. The local optical signal was collected by a tapered, uncoated optical fiber with a tip radius of about 50 nm and a tip-to-sample distance of about 10 nm. The resolution of the NSOM probe was ~150 nm. From the local intensity images obtained from the experiment, the higher-order field moments were calculated and the aforementioned linear dependence of field moments on the order n was confirmed. The experimentally obtained slopes $s(p)$ are compared with numerical results in Fig. 3. In the theory, the finite NSOM resolution is accounted for by estimating the field profile at a distance of 10 nm above the metal films and averaging the fields (not intensities) over a spatial area corresponding to the resolution limit of the probe. Figure 3 shows a similar trend with respect to p for both experiment and theory, with a clear minimum at p_c. The observed increase in slope away from p_c clearly indicates a localization transition at p_c. The analysis following Eq. (3) indicates that stronger SP localization is favored at noncritical metal concentrations, which leads to stronger local field fluctuations. The higher-order moments are more sensitive to those fluctuations, a fact that is manifested by the increase in the slope.

An increase of localization is also observed for longer wavelengths as per Fig. 3. This phenomenon is supported by both theory and experiment and has to do with the enhanced coupling at lower frequencies.[14] From Fig. 3 it is also clear that the increase of the local field fluctuations, manifested by the slope $s(p)$, holds for metal concentration up to some cutoff value $\Delta p_c = p - p_c$. The reason behind this phenomenon is the fact for a fixed incident frequency there is a minimum and maximum value of the metal concentration beyond which there are no resonating clusters present in the sample. Thus, in order for a SP mode to be excited by an incident field the maximum cluster size in the composite $l_m(p)$ should be larger than the limiting resonant size $l_r = a(|\varepsilon_m|/\varepsilon_d)^{\nu/(s+t)}$, where ν, s, and t are the critical exponents for the static conductivity, dielectric constant, and percolation correlation length, respectively.[16] According to the percolation theory $l_m(p) = a(p_c/|\Delta p|)^\nu$, which sets the cutoff metal concentrations $\Delta p_c(\lambda) = \pm p_c(\varepsilon_d/|\varepsilon_m|)^{1/(s+t)}$ [from $l_r(\lambda) = l_m(\Delta p_c)$].[16] The decrease in the slope for $|\Delta p| > |\Delta p_c| \approx 0.3$ is clearly manifested in Fig. 3.

The high-order local field moments M_n correspond to the multiphoton optical processes due to the excitation of SP resonances in the substrate. For instance, M_4 relates to the electromagnetic enhancement of Raman scattering provided that Raman-active molecules are deposited on the surface. Since the Raman scattering cross section in free space is extremely small, it is imperative that substrates be manufactured to optimize the electromagnetic enhancement. In accordance with the theory the field moment M_4 has a local minimum at p_c, which means that contrary to common belief, highly effective surface-enhanced Raman substrates can be manufactured at noncritical metal concentrations. Indeed, our numerical results based on Eq. (1) and presented in Fig. 4 show optimal electromagnetic enhancement at metal concentrations below the percolation threshold. Similar effects can be expected for other high-order optical processes such as hyper-Raman scattering, Kerr optical nonlinearity, and harmonic generation.

To conclude, we have theoretically predicted and experimentally observed an increase of the SP localization in random composites at noncritical metal concentrations. This effect runs opposite to the general notion that an increase of the number of scatters should lead to an increase in localization. The possibility for control over the localization of the collective electron response in complex metal-dielectric media could have important ramifications for a wide range of applications. Manipulation of the geometrical structure of the metal composites can be used to fine-tune the localization properties of the excited SP modes, which may considerably improve the enhancement of various linear and nonlinear optical processes.

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