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Impact of disorder on surface plasmons in two-dimensional arrays of metal nanoparticles

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We study the impact of disorder on the properties of surface plasmons (SP) in metal nanoparticle arrays and develop analytical expressions enabling us to ascertain the degree of localization and mixing between the SP states. We show that it might be advantageous to intentionally introduce a certain degree of disorder in order to engineer the improved sensors and detectors. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3152292]

Over the last decade significant attention has been devoted to the effects associated with field modification and enhancement in the vicinity of nanostructured metallic objects.[1] It is well understood that the enhancement of optical field is caused by localized surface plasmon (SP) modes and it has been demonstrated that diverse optical effects can be enhanced near the resonantly excited metal nanoparticles. Apart from isolated particles, ordered arrays of nanoparticles have also been studied at length,[2,3] enabling the observation of phenomena such as a well defined optical bandgap.[3] Most recently, it has been predicted[4] and observed[5,6] that spectrally narrow directional extinction resonances exist in ordered arrays of metallic nanoparticles separated by distances comparable to the free space wavelength of radiation. There exist a variety of applications for nanoparticle arrays with optical sensing probably being the most important. It should be noted that, however, for nanoparticles characterized by only a fraction of a wavelength in diameter but a separation of a full wavelength from each other, only a very small part of the sensor surface can actually experience the local field enhancement necessary for high sensitivity operation. Thus it would be desirable to use closely spaced arrays of nanoparticles[7,8] in which the electric field over most of the area would have been strongly enhanced.

In a periodic structure, momentum (the wavevector) is always preserved. Hence the SP modes can be described by a Bloch wave with a wavevector **q** in the Brillouin zone, as shown in Fig. 1(b) for the case of the square lattice in Fig. 1(a). The dispersion curve is shown in Fig. 1(c). The modes with $q<2\pi/\lambda$, i.e., less than the free-space wavevector, are radiative (bright) and can be coupled in and out at the angle $\theta(q)=\sin^{-1}(q\lambda/2\pi)$. Furthermore, the radiative decay rate $\gamma_r(q)$ of these modes is enhanced relative to the single nanoparticle decay rate γ_{r0}, as shown at top of Fig. 1(c), for the case of a lattice constant $a=\lambda/5$. The maximum enhancement in this case is given by $\gamma_r(0)\sim(4/3\pi)(\lambda/a)^2\gamma_{r0}$. At the same time, the majority of the modes [shown outside the small shaded disk with radius $2\pi/\lambda$ in Fig. 1(b)] are the nonradiative or dark modes that cannot be coupled outside. Thus in some applications (for example, the coupling of laser beams) ordered arrays offer the advantage of strength and directionality, while in other applications, such as fluorescence enhancement, the arrays are at a significant disadvantage since the energy from the excited molecules is coupled into dark modes and gets dissipated there.[9,10]

It should be noted that, however, once perfect order in the SP array has been violated, as shown in Fig. 1(a) with shaded circles, whether intentionally or not, a host of

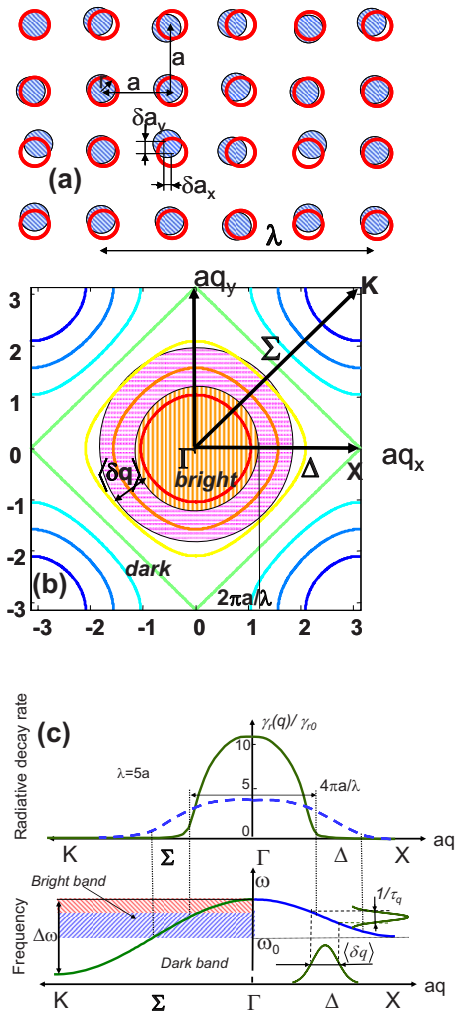

FIG. 1. (Color online) (a) Metal nanoparticle array: ordered (unshaded) and disordered (shaded). (b) Brillouin zone of (a) with surfaces of equal frequencies and the regions of bright SP for ordered (smaller shaded disk) and disordered (larger shaded disk). (c) Bottom: dispersion curves for SP with frequency and momentum spreads caused by disorder. Also shown is the extension of bright band with disorder. Top: radiative decay rate of ordered (solid) and 10% disordered (dashed line) SP modes.

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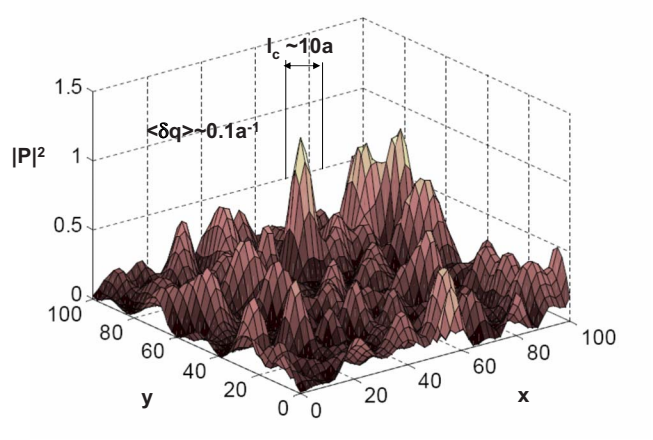

FIG. 2. (Color online) SP energy (square of polarization) in the disordered lattice.

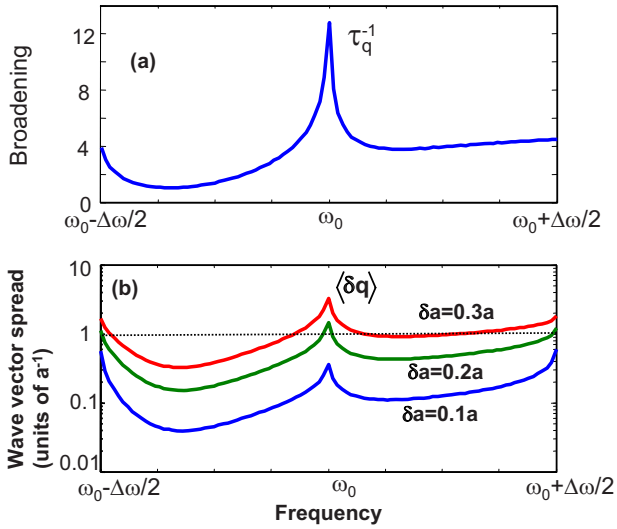

FIG. 3. (Color online) (a) Dispersion of scattering rate (broadening) of SP in units of $\Delta\omega(\delta a/a)^2$ (b) Dispersion of wavevector spread (in unit so inverse lattice constant) for 3° of disorder.

phenomena ensues that changes the optical properties dramatically. Most interestingly, these phenomena include localization[11] in which the SPs in the disordered array reacquire the properties of isolated nanoparticle SPs. A number of researchers have treated the SP localization problem,[12,13] but usually their work relied on numerical computations. While the numerical calculations, in principle, allow one to analyze the properties of each and every SP mode, from a practical point of view, one is only interested in the degree of localization of an average SP mode for a given frequency ω. For some applications, such as plasmonic waveguides, the issue of whether the modes are truly localized in the Anderson[11] sense, i.e., whether the plasmonic excitation can spread through the array (one- or two-dimensional) is critical. But when it comes to the absorption and emission of light in a given direction, only localization in the more narrow sense, as explained below, is important. The lack of translational symmetry in the disordered lattice of Fig. 1(a) causes mixing of SP modes with different wavevectors, and the "disordered SP" modes are spread out by $\langle \delta q \rangle$ in reciprocal space, as shown in Fig. 1(c). Due to the randomness of this disorder, the phases of different q-components are also random. Thus in the real space, such modes, as shown in Fig. 2, are characterized by the coherence length $\langle \delta l_c \rangle \sim \langle \delta q \rangle^{-1}$. It is only this characteristic length that influences the absorption and emission of the SPs, no matter whether the SP is moving or not. In this work we develop a simple yet rigorous and fully analytical theory that allows us to determine the spread of the SP mode in the wavevector space $\langle \delta q \rangle$ as function of the degree of disorder. Knowing $\langle \delta q \rangle$ for the "bright" modes allows one to estimate the angular spread of the light emitted by the array roughly as $\langle \delta\theta \rangle \sim \lambda \langle \delta q \rangle / 2\pi$, while for the dark modes $\langle \delta q \rangle$ one can show the degree to which they become partially luminous. These results are of high value when it comes to designing practical SP-enhanced devices.

We approach the SP disorder in a way similar to the way the alloy and isotope disorders are treated in condensed matter physics.[14] We start with a basic tight binding model for TM (vertically) polarized SP array modes in which the coupling between nanoparticles is only due to dipole-dipole interactions of nearest neighbors.[10] While imperfect, as shown in Ref. 15, this model is sufficient for explaining the main features in disordered lattices. Hence we obtain the dispersion [Fig. 1(c)]

$$\omega_{\mathbf{q}} = \omega_o + \frac{\Delta\omega}{4}[\cos(q_x a) + \cos(q_y a)], \tag{1}$$

where ω_0 is the isolated SP resonant frequency, and $\Delta\omega = 4\omega_0 r^3/a^3$ is a SP bandwidth. Such parameters as particle size, shape, and the distance between particles are subject to disorder and all can be treated in a similar fashion. Thus, in this letter we shall consider only the spacing disorder as a combination of two independent variables $\delta a_i = a_i - a$, $i = x, y$ characterized by identical correlation functions $\langle \delta a_i(\boldsymbol{r}-\boldsymbol{r}_1)\delta a_i(\boldsymbol{r})\rangle = (\delta a)^2 e^{-r_1^2/\Lambda^2}$ with correlation length Λ and the mean disorder δa. Their probability density in the reciprocal space is then also random and Gaussian $|\delta a_i|_k^2 = (\delta a)^2\Lambda^2 \exp(-\Lambda^2 k^2/4)$. Differentiating Eq. (1), we obtain the change in frequency as a function of the change in particle spacing, $\partial\omega_{\mathbf{q}}/\partial a_i = -\Delta\omega F_i/4a$, where $F_i = 3\cos(q_i a) + (q_i a)\sin(q_i a)$. We then apply Fermi's golden rule to evaluate the scattering rate of the SP as

$$\tau_q^{-1} = 2\pi A^{-1} \sum_{k,i} (\partial\omega_q/a_i)^2 |\delta a_i|_k^2 \delta(\omega_q - \omega_{q+k}), \tag{2}$$

where A is the total area. It is important not only for direct transitions between the states of equal frequency but also the Umklapp processes[14] to be included in this sum, hence the values of the scattering wavevector in Eq. (2) are limited to $k \leqslant \pi/a$. As in the alloy scattering theory, it is reasonable to assume that the correlation length of disorder is equal to a lattice constant a. Thus, the scattering terms are wavevector independent and

$$\tau_\omega^{-1} = (\pi/8)(\delta a)^2(\Delta\omega)^2\langle F_x^2 + F_y^2\rangle_\omega g(\omega), \tag{3}$$

where $g(\omega)$ is the density of states and averaging is done over the surfaces of constant frequency ω, as shown in Fig. 1(b).

For small values of q we obtain $\omega_q = \omega_{q=0} - \Delta\omega q^2 a^2/8$, $g(\omega) = 2/\pi\Delta\omega a^2$ $\langle F_x^2 + F_y^2\rangle_\omega \approx 18$. Therefore $\tau_0^{-1} = (9/2)\Delta\omega(\delta a/a)^2$, and for the full range of frequencies the results are shown in Fig. 3(a). As one can see, the scattering rate does not deviate significantly for a large range of frequencies near the top of the band but a peak near the

middle of the band occurs that has to do with the saddle point Van Hove singularity in the density of states near the *X*-points in the Brillouin zone. To estimate the wavevector spread one can use the uncertainty relation $\delta\omega_q\tau_q=1$ where the uncertainty of the energy $\delta\omega_q$ is related to the uncertainty of momentum via a Taylor expansion of the dispersion relation Eq. (1), $\delta\omega_q \approx \Delta\omega a^2\langle\delta q\rangle_q(2+\langle\delta q\rangle_q)/8$, as shown in Fig. 1(c), to obtain

$$\langle\delta q\rangle_q = \langle\delta q\rangle_0[\sqrt{1+(q/\langle\delta q\rangle_0)^2} - q/\langle\delta q\rangle_0], \tag{4}$$

where $\langle\delta q\rangle_0 \approx 6\delta a/a^2$ is the wavevector spread at the top of the band. For the realistically attainable minimum disorder of $\delta a/a \sim 1\%$, the coherence length $\langle\delta q\rangle^{-1}$ is on the order of 15 lattice spaces. However, when the disorder approaches 15%, the coherence length approaches a single lattice constant, indicating the complete localization of the low wavevectors (i.e., bright states).

For the whole band structure the wavevector spread is plotted in Fig. 3(b) as a function of frequency for three different values of disorder $\delta a/a$. At a moderate disorder of 10% the states near the band edges (Γ, K) and middle of the band (X) tend to be significantly more strongly localized than the rest of the states. This explains why in numerical analysis of Ref. 12 all four varieties (bright/dark, localized/delocalized) of SP states have been found to coexist. As the disorder increases to 20% and 30%, a majority of states are characterized by $\langle\delta q\rangle_q a \geq 1$, which indicates that they are localized on roughly one lattice space, causing the properties of the array revert to those of the assembly of uncoupled nanoparticles.

To illustrate the impact of disorder on the emission properties of the array we have plotted in the top of Fig. 1(c) (dashed lines) the radiative decay rate $\gamma_r(q)$ for the case of 10% disorder. In this case the mixing of "bright" and "dark" states has expanded the range of bright states [this is also illustrated in Fig. 1(b) as a larger shaded disk], while the peak decay rate has decreased accordingly. This expansion of the range of radiating states can have a highly beneficial effect in enhancing the luminescence of molecules placed in the array since the loss that occurs when the energy of molecules gets coupled into the nonradiating SP state[10] can be avoided. Also, the directionality of the array is reduced for light emitted (and absorbed) within an angle $\langle\delta\theta\rangle \sim \sin^{-1}(\delta a\lambda/a^2)$, which can be favorable for designing efficient wide angle absorbers for detectors and photovoltaic devices. Therefore, for the majority of practical applications it is probably far preferable to use completely randomized structures that can be readily fabricated by using 20%–30% disorder—not really surprising because randomization of surface had been routinely used to enhance light coupling in light emitting diodes, solar cells and detectors.

In conclusion, we have analyzed the impact of disorder in nanoparticles arrays and showed that one can engineer the degree of SP coupling to the outside world by changing the disorder, with important implications to the design of enhanced sensors and photodetectors.

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