Numerical Prediction of the Effect of Nanoscale Surface Roughness on Film-coupled Nanoparticle Plasmon Resonances

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ABSTRACT

Plasmon resonant metal nanoparticles on substrates have been considered for use in several nanophotonic applications due to the combination of large field enhancement factors, broadband frequency control, ease of fabrication, and structural robustness that they provide. Despite the existence of a large body of work on the dependence of the nanoparticle plasmon resonance on composition and particle-substrate separation, little is known about the role of substrate roughness in these systems. This is in fact an important aspect, since particle-substrate gap sizes for which large resonance shifts are observed are of the same order of typical surface roughness of deposited films. In the present study, the plasmon resonance response of 80 nm diameter gold nanoparticles on a thermally evaporated gold film are numerically calculated based on the measured surface morphology of the gold film. By combining the measured surface data with electromagnetic simulations, it is demonstrated that the plasmon resonance wavelength of single gold nanoparticles is blueshifted on a rough gold surface compared the response on a flat gold film. The anticipated degree of spectral variation of gold nanoparticles on the rough surface is also presented. This study demonstrates that nanoscale surface roughness can become an important source of spectral variation for substrate tuned resonances that use small gap sizes.

Keywords: gold particle resonance, surface-tuned resonances, nanoscale roughness, surface roughness

1. INTRODUCTION

Understanding the plasmonic response of metal nanostructures is an important step toward engineering plasmonic structures with optimized resonance properties. Several frequency controlled plasmon resonance structures utilize electromagnetic coupling between closely spaced nanostructures to shift plasmon resonances. The preparation of such structures generally involves costly and time consuming fabrication techniques such as electron beam lithography. Substrate-based tuning of nanoparticle plasmon resonances on the other hand makes use of the coupling between a nanoparticle and induced polarization in the substrate.[1,2] Since the resonance response depends on substrate composition or deposited layer thickness only, the need for precise alignment between nanostructures is eliminated. The plasmon resonance of substrate-controlled or 'film-coupled' nanoparticles can be adjusted simply by depositing particles on different substrates. Several studies have reported a large resonance tuning range and strong predicted electric field confinement of film-coupled nanoparticles.[3–6] For small particle-substrate separations, the typically dipolar plasmon resonance of spherical particles is perturbed by the substrate, resulting in hybridized gap plasmon modes with multipolar character and a maximum field amplitude near the contact point with the substrate.[7–9] Film-coupled plasmon resonant structures can be prepared using chemically synthesized metal nanoparticles and a thin metal or dielectric layers prepared using standard deposition techniques. Therefore, making film-coupled plasmon resonance structures is simpler, less costly, and less time consuming than lithography-based nanostructure fabrications. This relative simplicity also enables reproducible resonance control as well as advantages in structural and thermal stability of the structure.[6]

Based on the simplicity of the fabrication of film-coupled plasmon resonant systems, it could be expected that particle size and shape variations would be the main contributing factors to variations in metal nanoparticle resonance spectra. However, due to the high mode confinement of gap plasmons in film-coupled nanoparticle systems nanoscale surface roughness could also play an important role. While gap plasmon resonances have been investigated in numerous studies, a thorough investigation of the effect of surface roughness on the spectral variation of gap plasmon resonances is lacking. In this study, we present a numerical approach to identify how roughness influences nanoparticle resonances, and to predict the magnitude of this effect in realistic experimental systems. In particular, we study the effect of surface

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roughness of a thermally evaporated gold film on the resonance wavelength of 80 nm diameter single gold nanoparticles on a gold substrate. The analysis is based on the measured surface morphology of a thermally evaporated gold film as characterized using Atomic Force Microscopy (AFM), combined with numerical simulations of representative surfaces.

2. SUBSTRATE PREPARATION AND CHARACTERIZATION

2.1 Sample preparation and atomic force microscopy

A gold film was deposited by thermal evaporation (Edwards FL 400 thermal evaporator). A 2 nm thick chromium wetting layer was evaporated onto a glass cover slip (Thermo Scientific), followed immediately by thermal evaporation of a gold film with a measured thickness of 48.7 ± 0.5 nm as determined by variable angle spectroscopic ellipsometry (Woollam M2000). The surface morphology of the as-deposited film was analyzed using AFM. Figure 1(a) shows an AFM image of the gold surface with an area of 1 μm × 1 μm. The root mean square (RMS) roughness in the measured image is 1.17 nm. While this RMS roughness appears negligibly small compared to the particle diameter of 80 nm, as we will show below these small height variations can significantly affect the total spectral response of the system. For comparison, the solid white circle in Fig. 1(a) shows the Au nanoparticle size of 80 nm as assumed in this study. This is a typical size used in experiments on substrate-tuned nanoparticle resonances.

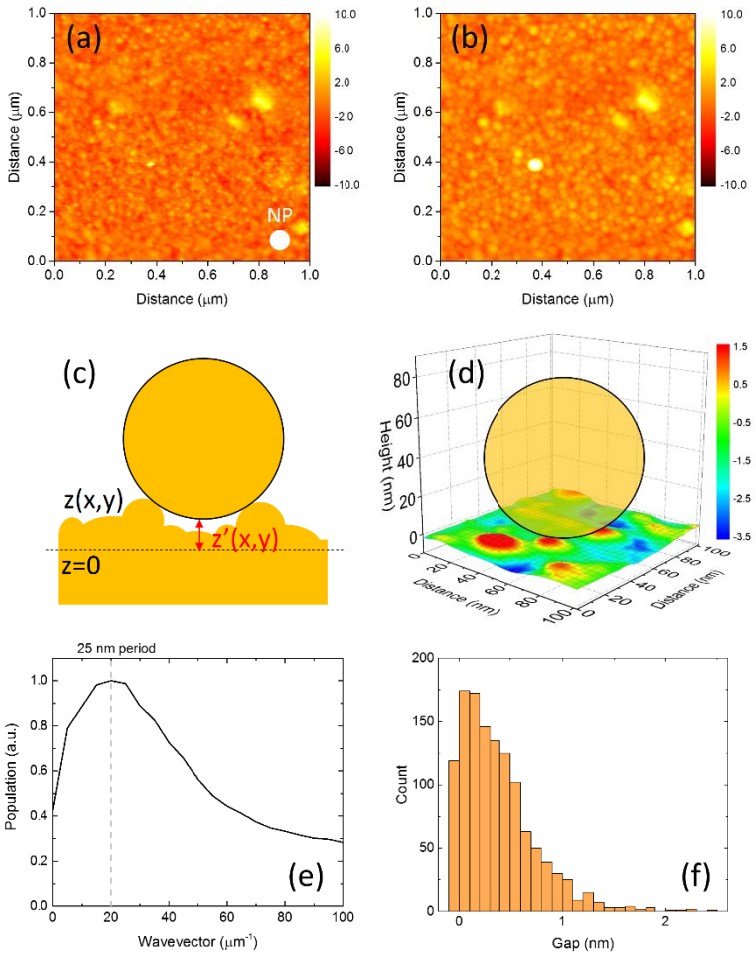

Figure 1. (a) Atomic force microscopy image and (b) corresponding processed data showing the height values that an 80nm particle could occupy on this surface. (c) A sketch of the method used for finding allowed particle height values. (d) An AFM image of the gold surface with a semi-transparent 80 nm diameter gold nanoparticle superimposed at a randomly picked local height minimum. (e) Normalized distribution of spatial wavevector population of the gold surface roughness seen by a gold particle. (f) Histogram of likely particle-substrate gap sizes.

2.2 Numerical characterization

In order to predict the scattering resonance spectrum of single gold nanoparticles on a rough substrate, the exact local environment of each particle must be known, however this is not possible to determine with most analysis techniques. For example, AFM and scanning electron microscopy only reveal the substrate around the particle, but not under it. Cross-sectional transmission electron microscopy of a sample section requires destruction of the sample and usually only offers one view (single side view) of the immediate particle environment. Since the exact three-dimensional local environment is not easily obtained and varies from particle to particle, here we extract likely local environments based on the measured surface morphology. Deposition of gold nanoparticles for the preparation of surface-tuned plasmon resonance structures commonly involves drop coating a colloidal solution of gold nanoparticles, followed by drying in flowing air or flowing nitrogen. In the present study it is assumed that the particles settle in local height minima on the gold, driven by capillary forces during the sample drying process. The possible local minima are not simply the local minima seen in the raw AFM data but rather the local height minima that can be accessed by the finite-size gold nanoparticles.

To find possible local height minima, an algorithm was developed that converts measured AFM data to a virtual surface representing all z-positions that can be occupied by an 80 nm diameter nanoparticle. The algorithm places the particle at each x,y coordinate, and lowers the 80 nm diameter particle until it comes into contact with any part of the scanned surface. As such the algorithm mimics an AFM scan of the surface if the surface was mapped with an AFM tip with a 40 nm tip radius. Figure 1(b) shows the processed 3D surface corresponding to the AFM data in Fig. 1(a). The over 1200 local minima in this graph represent likely final locations of the Au nanospheres. Figure 1(c) shows a 2D sketch of a local particle height minimum obtained by this method.

Figure 1(d) shows AFM data of a 100 nm × 100 nm section of the gold surface at a randomly picked local minimum out of the 1200 local minima found, with a rendering of an 80 nm diameter nanoparticle superimposed at the local minimum. It can be seen that the particle deposited at this local minimum is supported by three contact points as the result of the surface roughness. This is by far the most likely configuration (~90 % of all minima), with the other likely configuration being a nanoparticle with a single contact point (10% of minima) Even knowledge of the possible locations, the presence of one or three contact points, and the particle substrate separation at these minima does not paint a complete picture. In order to predict typical resonance spectra of particles in these local minima, the typical position of the three contact points must be estimated. To find this information, the surface roughness was spectrally analyzed. In particular, the periodicity of the protrusions on the surface was determined to be 25 nm by determining the most prevalent spatial wavevector present in the rough surface. This was done by carrying out a two dimensional Fourier transform of the AFM image in Fig. 1(a) and angularly integrating the two-dimensional Fourier amplitude at each wavevector magnitude to find the total population of a specific wavevector presents on the surface. Figure 1(e) presents the resulting normalized plot of the wavevector population as a function of the wavevector magnitude. The predominant period was used as typical separation between the protrusions making up the contact points. The local environment is thus assumed to be made up of three spherical protrusions with a 25 nm lateral separation. These protrusions can create a gap separating the deposited nanoparticle from the gold surface, see the schematic in Fig. 1(c). Variations in these local gaps could introduce spectral variations in the plasmon resonances of single gold nanoparticles on rough substrates. For this reason, expected separations were extracted from the particle height map in Fig. 1(b). Figure 1(f) shows the thus obtained histogram of possible gaps between the particle and the substrate at the local minima in Fig. 1(b). Since only 10% of the local minima has zero particle-substrate separation, the optical response will be dominated by particles supported by three contact points with a resonance affected by the gap size. The histogram in Fig. 1(f) shows that the gap sizes range from a few angstroms to as much as 2 nm, which is anticipated to result in significant particle-to-particle variation of the plasmon resonance response.

3. NUMERICAL SIMULATION

The surface morphology of the deposited gold film was approximated for numerical simulations based on the analysis discussed above. Figure 2(a) and (b) present a top view of the gold surface and a perspective view of an 80 nm diameter gold nanoparticle on the gold surface created in electromagnetic simulation software,[10] respectively. The surface has three protrusions making up an equilateral triangle with 25 nm sides matching the predominant experimentally observed spatial periodicity of the surface roughness. Each protrusion is represented by a gold sphere with a radius of 32 nm ($0.8 \times R_{NP}$) protruding from the gold film. The gold dielectric function was taken from literature.[11] The surface is assumed to be coated with a 0.5 nm thick organic layer (n=1.55) to represent a surface layer of remaining stabilizing organic ligands typically present in colloidal nanoparticle suspensions. A gold nanoparticle is placed on these gold protrusions, representing a nanoparticle at a typical local height minimum. The height of these protrusions affects the particle-substrate separation, similar to what happens on a rough surface. A plane wave with TM polarization and an angle of incidence of 77° relative to the surface normal was used as the excitation source, matching a typical angle used in darkfield scattering spectroscopy.

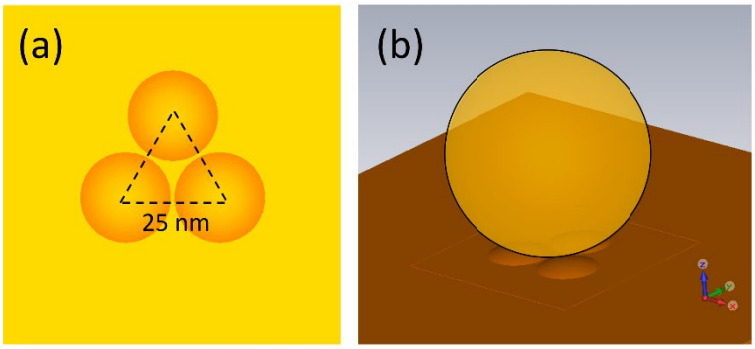

Figure 2. (a) Top view of the gold surface model showing three protrusions mimicking the surface roughness and (b) perspective view of an 80 nm diameter gold nanoparticle on the gold surface.

4. RESULTS AND DISCUSSION

In order to monitor changes in the plasmon resonances of gold nanoparticles on gold surfaces with different gap sizes, the electric field magnitude at the center of the particle was probed as a function of excitation wavelength. The electric field at the center of the particle has been observed to give a reasonable prediction of the scattering signal strength in surface-coupled particles.[5] Figure 3(a) presents the simulated electric field magnitudes at the center of a gold nanoparticle for geometries that produce gap sizes in the range 0 nm – 2 nm. The spectra show a clear resonance peak and a blueshift in the gold nanoparticle resonance wavelength from 814 nm to 740 nm as the gap size is increased. The shift in the resonance wavelength becomes less pronounced at larger gap size. This suggests that the effect of surface roughness on surface-tuned nanoparticle plasmon resonances is most critical for small particle-substrate separation. Figure 3(b) shows the simulated peak resonance wavelengths (solid squares) as a function of a gap size of the electric field spectra in Fig. 3(a) together with an empirical fit to the data (solid line). The resonance wavelength in nanometers can be fit with a simple exponential function $\lambda_{res}(d) \approx 743 + 72 \times e^{-(d/0.2)}$ where λ_{res} and d are the resonance wavelength and gap size in nm, respectively. Based on this formula and the histogram in Fig. 1(d), the predicted mean resonance wavelength and standard deviation of plasmon resonance wavelengths of 80 nm diameter gold nanoparticles on the thermally evaporated gold surface in Fig. 1(a) are calculated to be 767 nm and 23 nm, respectively. The mean resonance wavelength and one standard deviation from the mean are represented by the black dashed lines and shaded gray regions in Fig. 3(a) and 3(b). The predicted mean resonance wavelength is 47 nm shorter than the resonance wavelength of a particle on a flat gold film indicating that surface roughness can significantly affect plasmon resonances of gold nanoparticles. The top and bottom insets on the right of Fig. 3(b) show images of a gold nanoparticle on an ideal flat gold film and a gold film with rough surface, respectively. The spectral variation found in this study is comparable to spectral variations observed in other film-coupled nanoparticle plasmon resonance studies.

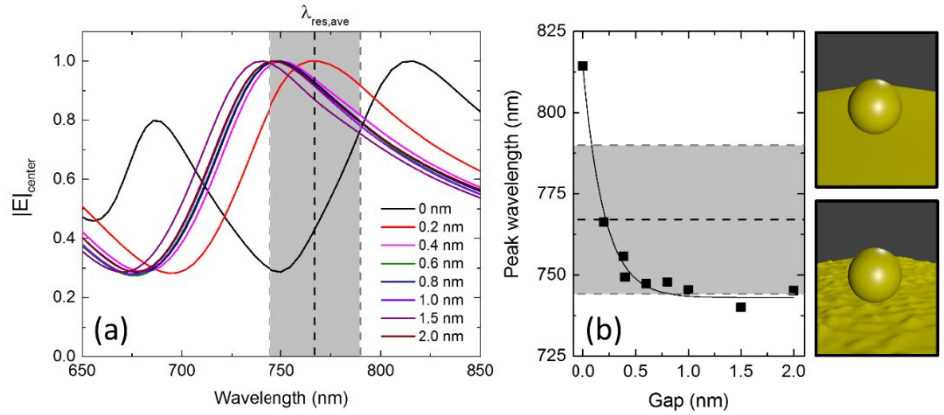

Figure 3. (a) Simulated electric field magnitude at the center of a gold nanoparticle for local environments with different gap sizes. (b) Simulated (solid squares) and empirical fit (solid line) to the peak resonance wavelength of a gold nanoparticle at different gap sizes. The black dashed lines and shaded gray areas indicate the mean wavelength and predicted standard deviation of the plasmon resonance of a gold nanoparticle on a rough gold film based on likely gap sizes found from experimental data.

5. CONCLUSION

A numerical procedure is presented for predicting the plasmon resonance wavelength and the spectral variation of the resonance wavelength of gold nanoparticles deposited on a rough gold film, based on experimental AFM data. It was shown that surface roughness of a thermally evaporated gold film is sufficient to create gaps between the deposited gold nanoparticles and the gold surface. By analyzing possible gap sizes statistically, resonance wavelength shifts and spectral variations are predicted. The approach shown in this study can be extended to other materials and particle sizes. Such predictions are useful in designing surface-tuned plasmonic systems and predicting the reproducibility of the resulting systems.

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