

Theoretical analysis of the effective optical properties of gold-nanoparticle-loaded polymer films and their transition from surface to bulk values with varying thickness

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Systems of resonant gold nanoparticles embedded in a dielectric matrix have been studied for a long time from a fundamental point of view [1], and present interesting optical properties. The optical response of such systems in the visible region of the spectrum is dominated by the Localized Surface Plasmon Resonance (LSPR) of the particles. As a consequence, by varying the actual amount of nanoparticles, effective properties like permittivity or optical index of the composite film can be tuned, and at high enough loading fractions, they can exhibit large values or negative regions in the neighborhood of the LSPR. We study this system as a first step towards more complex systems with highly-engineered resonant particles which could give birth to metamaterial-type responses (e.g., double negativity).

Interestingly, even a simple system like this one still presents significant challenges in the understanding of the effective optical response. On the particle scale, the exact position of the LSPR directly depends on the dielectric function of the metal and matrix but also on the particles' shape [2]. For very small ones (around 10nm in diameter), confinement effects become important and there still exists uncertainty about the correct dielectric function that should be used. On the global scale, the volume fraction (density) and the spatial distribution of the particles in the matrix (dispersed in volume or located on a substrate) also strongly alter the LSPR spectrum and hence the optical response of the whole system. All these aspects should be integrated correctly into a suitable model. For dilute bulk geometries (3D), where particles are far from the substrate supporting the film, effective medium approaches such as the Maxwell-Garnett mixing rule, have shown to be quite satisfactory [3]. On the other hand, 2D-like systems with nanoparticles directly deposited on substrates require more sophisticated modeling tools. These have been developed during the 1970's and 1980's [4] and were later applied to determine for instance surface densities from spectroscopic ellipsometry measurements [5].

In this work we analyze the optical response of polymer films doped with gold nanoparticles (AuNP). Different spectra are obtained by means of UV-vis transmission spectroscopy and ellipsometric spectroscopy for different polymer film configurations: monolayer or volume dispersion of AuNP, supported either by a transparent (glass) or a reflective substrate (Si/SiO_2). Comparison of the results for the doped polymer film with those obtained for AuNP suspended in water shows strong differences in the width of the plasmon peak. The inclusion of AuNP's in the polymer matrix tends to broaden this peak. This effect can be related to the modified dielectric environment of the nanoparticles and possibly to some amount of aggregation occurring during the process of polymerization [6].

A model is proposed which takes into account the effect of the electron confinement, size polydispersity due to chemical synthesis and the substrate on the effective optical properties. In the case of thin polymer films (particle monolayers), interaction with the substrate has to be introduced by means of the image method. A modified polarizability is obtained by keeping only the dipole term in the expansion. With these physical ingredients, we propose a simple generalization of the Maxwell-Garnett mixing rule where we include both "volume" particles, and "surface" particles with modified polarizabilities (see figure 1).

This extended Maxwell-Garnett model brings several noteworthy features: first, it allows us to study mixed 2D-3D films, by describing continuously the evolution of the effective electromagnetic properties when the thickness of the composite film is varied from a fully 2D-situation (monolayer of nanoparticle on a substrate) to a fully 3D-situation (thick films), passing through all intermediate cases. This is interesting as, to the best of our knowledge, only purely 2D or purely 3D models were available to date. Second, our model also allows to separately change the amount of particles in the bulk of the material and the amount sitting at the surface of the substrate. We are therefore able to study the influence of repulsive, attracting or neutral substrates over the global electromagnetic response of the composite material.

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References

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Figures

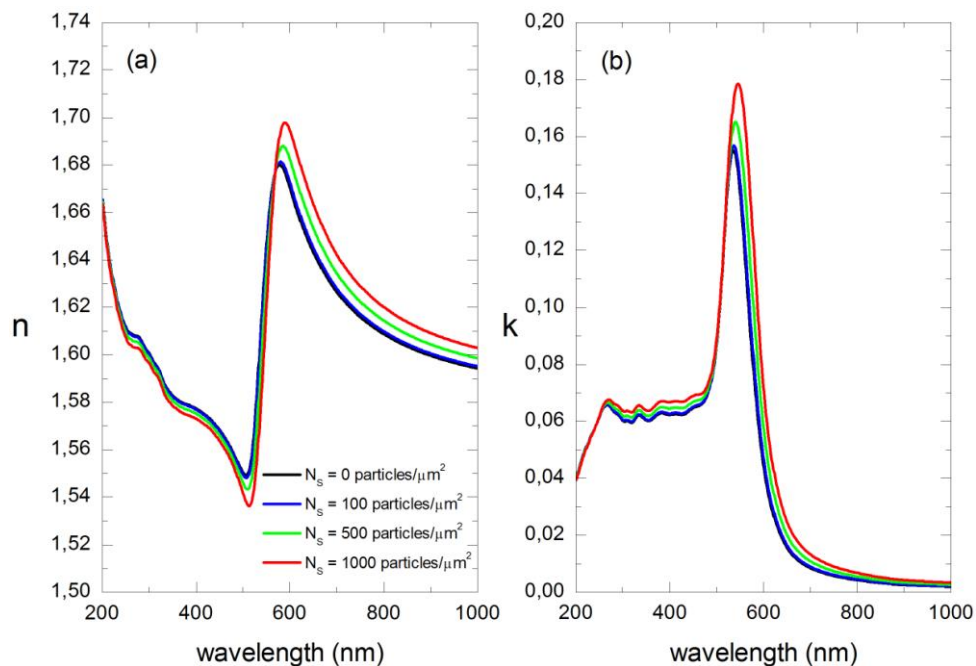


Figure caption

Figure 1 : (a) real part and (b) imaginary part of the refractive index. The curves were produced by applying the Maxwell-Garnett formula considering gold spherical inclusions in a polymer matrix. The volume fraction of the AuNP is 3%. For $N_s=0$, no substrate effect is taken into account.