Effective optical properties of dilute and dense polymer-gold nanoparticle films: theory and experiments

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Abstract

We study the effective optical properties of composite films made of 14-nm spherical gold nanoparticle in a polymer matrix, both in dilute (5% gold fraction) and dense (20%) regimes. Optical indices and permittivities are extracted from spectroscopic ellipsometry measurements and show effective resonant properties around the plasmon resonance, exhibiting effective negative permittivity for dense samples in a finite frequency range (finite-band metallic behaviour). Measurements are compared to Maxwell-Garnett (MG) predictions: we show that the classical MG formula does not reproduce the experimental results, even in the dilute regime, due to nanoagregation effects in the samples which entails couplings between particles. Since couplings create deformations of the polarizability tensor of the individual particles, we propose to take them into account in an empirical way using a modified MG formula based on a distribution of ellipsoids. We show that this modified Maxwell Garnett model works sucessfully, allowing for good fits of the experimental data in the dilute regime (using a distribution of ellispoidal polarizabilities centered on a mean isotropic polarizability) as well as in the dense regime up to 20% (using polarizability distribution centered on a mean ellipsoidal polarizability).

1. Introduction

Developments in designs over the past couple of years have brought the field of metamaterials into a stage where, besides usual lithography-based approaches, new "bottom-up" fabrication techniques based on nanochemistry and material science can now be effectively explored [1]. Expected benefits from bottom-up approaches include assembling true three-dimensional (3D) metamaterials or natively synthetizing resonators with sizes appropriate for the optical range. In the present work, we study the effective optical properties of composite materials made of spherical gold nanoparticles (GNP) randomly dispersed into a polymer host matrix. Such composite films, for high enough filling fractions, are expected to display an adjustable, near-zero or negative effective permittivity band around the particle plasmon resonance.

2. Experimental results

The host medium of our composite material is a hydrosoluble polymer (poly-vinyl alcohol) with refractive index $n = 1.5$ and weak absorption ($k \approx 0$). GNPs are synthesized in water following a classical protocol, and are consistently spherical with an extremely well-defined diameter of 14 nm. Films are made by spin-coating mixed dispersions of polymer and GNPs onto silicon wafers. Experimental parameters can be adjusted so as to control both the thickness and GNP filling fraction f of the obtained composites. Dilute films are obtained from a one-shot spin-coating process, while dense films are obtained from multiple spin-coating upon the same substrate.

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The optical properties are obtained from variable-angle spectroscopic ellipsometric measurements, and the complex optical index $n + ik$ is extracted using a suitable ellipsometric model and a lamba-by-lambda numerical inversion procedure. The complex permittivity of the film ε is then calculated from the complex index.

Experimental results are shown in Figure 1 for two typical samples in the dilute ($f \simeq 6\%$) and dense ($f \simeq 20\%$) regimes. In the dilute sample [Figure 1 (a) and (b)], the plasmonic resonance of the GNPs can be distinctly observed, but has a small amplitude. For the dense sample [Figure 1 (c) and (d)], the resonance has a much greater amplitude and the response displays a near-zero permittivity region in the short wavelength range which becomes negative around 600 nm with $\mathrm{Re}(\varepsilon)\big|_{\mathrm{min}} \simeq -2$. This is interesting behaviour, as it means that the composite has a hybrid macroscopic optical response: it responds like a metal over a finite frequency band, and like a dielectric elsewhere. Finally, we also note that both resonances have a significant linewidth, with more or less redshifted resonance wavelengths, denoting the presence of couplings between GNPs in the sample.

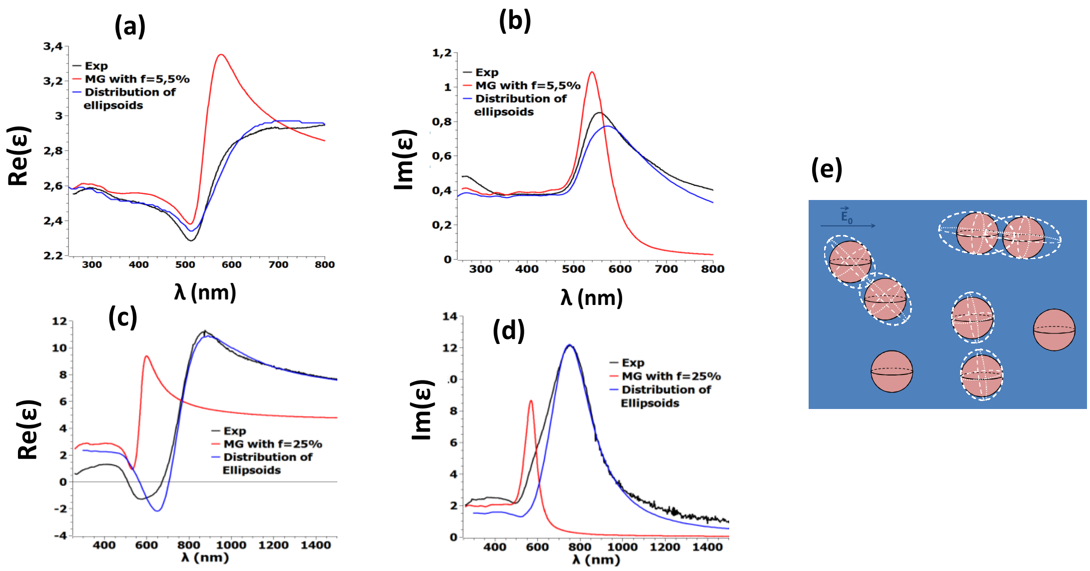

Fig. 1: (a) and (b) Real and imaginary parts of the permittivity versus wavelength λ for a dilute sample with $f \simeq 6\%$. Black line: experiment; Red line: classical MG model; Blue line: modified MG with distribution of ellipsoidal polarizabilities. (c) and (d) Real and imaginary parts of the permittivity for a dense sample with $f \simeq 20\%$. Black line: experiment; Red line: classical MG model; Blue line: modified MG with distribution of ellipsoidal polarizabilities. (e) Ellipsoidal polarizabilities as empirical representations of electromagnetic couplings between neighbouring particles.

3. Modified empirical MG model for coupled particles

We tried to reproduce our experimental data with the help of the classical MG law [2]. However, as Fig. 1 shows (red lines), the MG predictions are mediocre for the dilute sample and completely off the mark for the dense one. This is clearly due to the couplings taking place inside the samples, which are due to structural nanoagregation effects. As depicted schematically in Fig. 1 (e), in an empirical way, couplings between particles can be seen as deforming the initially isotropic polarizability of the nanospheres into ellipsoidal ones; this is a reflection of the local field distorsions induced by the couplings. Therefore, a simple-minded approach to improve the model is to introduce ellipsoidal polarizabilities in the MG model: we take a distribution of ellipsoids to represent the variety of couplings at work (we choose a log-normal-like distribution), and we assume that the orientations of the coupling-induced ellipsoids are random. The effective permittivity $\varepsilon_{\mathrm{eff}}$ of the composite given by the modified MG model then takes the

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simple form [5]:

$$\varepsilon_{\text{eff}} = \frac{(1-f)\varepsilon_{\text{m}} + \beta f \varepsilon_{\text{p}}}{(1-f) + \beta f} \tag{1}$$

where ε_{m} is the permittivity of the host matrix (polymer), ε_{p} is the permittivity of the GNPs (using the dielectric function of gold [3] corrected for electron confinement [4]) and β is an integral moment of the chosen ellipsoidal distribution $P(L_1, L_2)$ [5]:

$$\beta = \iint P(L_1, L_2) \frac{\lambda_1 + \lambda_2 + \lambda_3}{3} \text{d}L_1 \text{d}L_2 \tag{2}$$

where L_1, L_2 and L_3 are the depolarization factors defining ellipsoids along directions 1 and 2 (note that $L_1 + L_2 + L_3 = 1$) Furthermore, the integral involves the parameters $\lambda_j = \varepsilon_{\text{m}} / \left[\varepsilon_{\text{m}} + L_j(\varepsilon_{\text{p}} - \varepsilon_{\text{m}})\right]$ where $j = 1, 2, 3$.

We see in Fig. 1 (blue lines) that this modified MG model reproduces much better the experimental data. For the dilute sample, there is only two fitting parameter which are the global gold filling fraction f and the width of the log-normal ellipsoidal distribution; the ellipsoidal distribution is centered on the undisturbed, isotropic polarizability of the individual nanospheres. For the dense samples, because couplings are much stronger, it is necessary to center the ellipsoidal distribution on a mean ellipsoidal polarizability, reflecting the fact that no particle is free from coupling, even in average. The proper mean ellipsoid is first found by adjusting its resonance frequency on the observed experimental resonance, then an ellipsoidal distribution is taken around this mean ellipsoid, and the distribution width is adjusted for the theoretical curve to fit the experimental curve. Hence, for the dense samples, there are four free parameters: the total gold filling fraction f, the two depolarization factors of the mean ellipsoid, and the width of the distribution.

4. Conclusion

We have studied the optical properties of both dilute and dense samples of polymer-GNP composites using spectroscopic ellipsometry. Experimental results show resonant variations of the composite permittivity around the plasmon frequency, which is more pronounced as the filling fraction in GNP increases. For samples with filling fraction $f \simeq 20\%$, a finite region of negative permittivity is observed, conferring the composite with a metal-like behaviour over a finite frequency range. A variant of the classical MG model based on a distribution of ellipsoidal polarizabilities has been proposed to take into account, in an empirical way, the effects of interparticle couplings in both dilute and dense samples. The proposed model makes it possible to reproduce the experimental data in a satisfying manner.

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