Bottom-up fabrication of metamaterials by metallic nanoparticle self-organization

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Abstract

In this paper, the bottom-up fabrication of metamaterials by self assembly of metallic nanoparticles into spherical clusters is discussed. The refractive index of silver nanoparticle composites with different concentrations, from dispersed to randomly packed nanoparticles, is measured by spectroscopic ellipsometry, demonstrating high permittivity values in the visible. As a potential metamaterial building block, nanoparticle spherical assemblies are prepared by a method based on oil in water emulsion and their optical properties are characterized.

1. Introduction

Owing to the wide range of new applications offered by optical metamaterials (MM), an important effort has been devoted to their practical realization over the past years. Due to the weak magnetic response of most natural materials, the most critical task was to tailor the permeability of such MM, by a proper design of its constituents. Several structures have already been implemented successfully to tackle this problem. They are all based on subwavelength conducting inclusions with complex geometries like split rings or fishnets. Despite these successful achievements, current metamaterials still suffer from several drawbacks inherent to their design and fabrication process. Indeed, due to their complex architectures, their fabrication requires expensive and time-consuming nanofabrication technologies such as e-beam and ion beam lithography or direct laser writing. Furthermore, these top-down methods usually only allow the fabrication of planar arrangements which makes it difficult to fabricate a true bulk and isotropic metamaterial. An alternative design that has been far less explored but which could overcome these limitations is based on the interaction of light with small dielectric objects like nanospheres. In this case, the magnetic activity stems from the strong displacement currents that can be excited in such meta-atoms for specific Mie-resonance frequencies, provided that the refractive index contrast with their environment is strong enough. To fulfil this condition, it was recently suggested[1] that metallic nanoparticles could be used as the high index material to form such metaatoms(Figure 1).

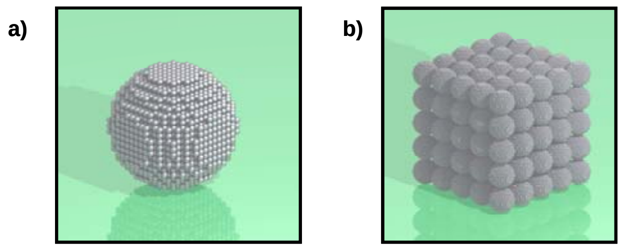

Fig. 1: Sketch of (a) a meta-atom based on the self assembly nanoparticle into spherical clusters and (b) the resulting metamaterial,taken from [1].

This approach lends itself perfectly to bottom-up fabrication techniques based on colloidal self organization and should allow an easy implementation of a bulk isotropic metamaterial, given the spherical geometry of the inclusions. Within the framework of the European project Nanogold[2] ,we aim to explore in detail the concept of metallic NP based metamaterials from design to fabrication. In this contribution, we first evaluate the potential of silver NP composites for metasphere fabrication by measuring experimentally their complex refractive indices at different NP concentrations. We then prepare and characterize NP metaspheres using a method based on droplet formation in oil-in-water emulsions.

2. Refractive index of silver nanoparticle composites

Silver NP dispersions with different NP content were studied by spectroscopic ellipsometry and modelled using Mie theory. Silver NPs (10 nm diameter) dispersed in tetradecane at high concentration (Figure 2a) as well as dry thin films prepared by spin coating (Figure 2b) were investigated. In all cases, a strong dispersion in the permittivity is observed around the NP plasmon band. As expected, the refractive index clearly depends on the volume fraction f occupied by the NPs. When they are sufficiently densely packed like in the randomly packed film, values of the refractive index as high as 4-5 are obtained. Mie based simulations indicate that a metamaterial with a permeabilty significantly lower than unity could be obtained by forming close-packed metaspheres with such NPs. In order to reach negative values, it would be however necessary to further increase the permittivity of the NP composite by increasing the NP diameter for instance.

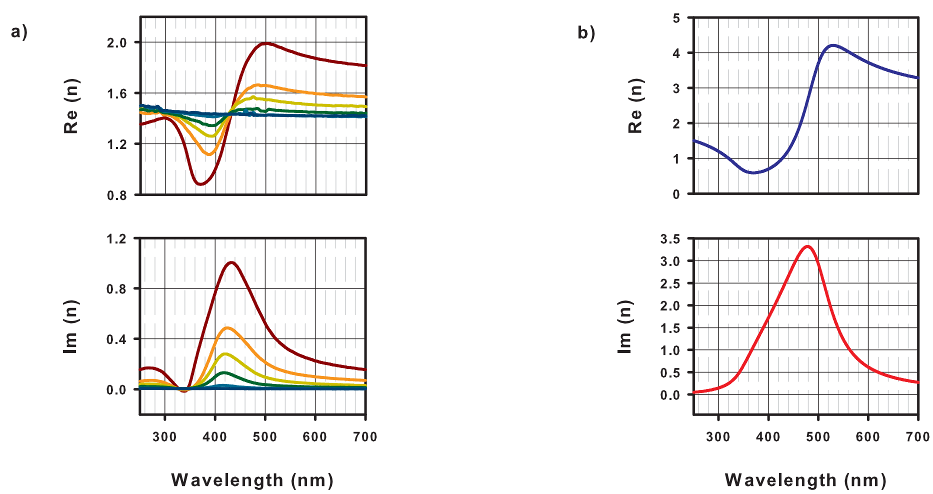

Fig. 2: Refractive index of silver nanoparticles for different filling fractions f: in liquid dispersions (a) and a dry randomly close packed thin film(b)

Another aspect shown by these data is the strong redshift of the plasmon band as the NP content is increased (from 400 nm at low concentration to 480 nm for the dry films). This shift can be explained by the near-field coupling between NPs that occur as their separation becomes comparable to their size (for, instance the interparticle distance in the most concentrated tetradecane solution is around 12 nm). Note that such opaque dispersions are hardly measurable in transmission due to their strong absorbance (OD>>1).

3. Emulsion based fabrication of NP metaspheres

In order to fabricate NP metaspheres, we used a method inspired from the concept of oil in water emulsions[3]. The silver NP dispersion in tetradecane (i.e the oil phase) was added drop-wise, under constant mechanical stirring, to an aqueous solution contaning sodium dodecylsulphate (SDS) as a surfactant. Following such a treatment, small oil droplets containing NPs are formed in the water phase and surfactant molecules arrange themselves at the water-oil interface to lower the surface tension. Optical and SEM characterization (Figure 3a and 3b) confirmed the formation of spherical droplets covered by SDS, with sizes on the order of a few hundreds of nanometers. SEM images of fractured droplets tend to indicate that NPs have migrated to the droplet interface forming hollow sphere assemblies.

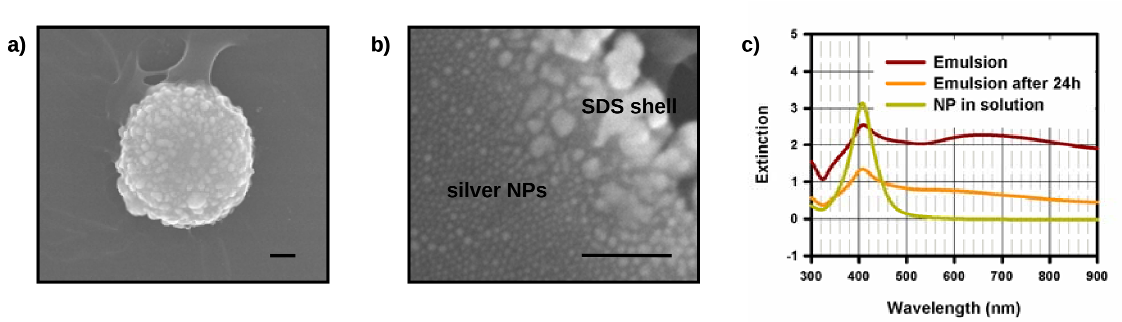

Fig. 3: (a) SEM image of an emulsion droplet. (b) Fractured droplet showing the SDS surfactant shell and a closed packed silver NPs along the shell. Scale bars: 100 nm (c)Extinction spectra of the emulsions

The extinction spectrum of the raw emulsions (Figure 3c) still show the characteristic plasmon band of silver NPs around 400nm, indicating that isolated NPs are still present in the solution. However, a broad extinction peak around 650 nm, associated with the excitation of the droplets' Mie resonances is also present. Following the sedimentation of the biggest droplets, this peak shifts to smaller wavelength as expected for smaller droplets. The origin of this peak can be reasonably attributed to the fundamental magnetic Mie resonance of the NP doped droplets. Hence, an assembly of such metaspheres could be used to form a magnetic metamaterial at optical frequencies. However, the emulsification process still needs to be improved to obtain monodisperse metaspheres with proper dimensions and in sufficient quantities to fabricate a real metamaterial.

4.Conclusion and perspectives.

The present results confirm the ability of NP composites to be used as a starting material to form magnetic meta-atoms, paving the way to a bottom-up approach for metamaterial fabrication. The high permittivity of NP composites has been confirmed by ellipsometry and a bottom-up method based on emulsion technology has been successfully tested for the fabrication of spherical NP assembly.

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References

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