Influence of Disorder on the Optical Properties of Spherical Plasmonic Nanoclusters

Andrea Vallecchi and Matteo Albani
Dept. of Information Engineering
University of Siena
Siena 53100, Italy
andrea.vallecchi@unisi.it; matteo.albani@dii.unisi.it

Filippo Capolino
Dept. of Electrical Engineering and Computer Science
University of California-Irvine
Irvine, CA 92697, USA
f.capolino@uci.edu

***Abstract*—The optical response of irregular spherical nanoclusters (NCs) are studied by Monte Carlo simulations. Deviations from nominal arrangements are considered by introducing either randomly variable sizes of the constituent particles or random displacements of particle locations around the NC core. The impact of disorder on NC resonances is examined by decomposing the scattered fields in terms of contributions of electromagnetic multipoles, such as electric and magnetic dipoles, quadrupoles, and higher order moments.**

I. INTRODUCTION

Spherical clusters of self-assembled plasmonic particles can be used as building blocks for magnetic and negative index materials at optical frequencies [1]. NCs are formed by a number of metallic nanoparticles attached to a central dielectric core. This type of arrangement can force the electric field to circulate in the plane orthogonal to the incident magnetic field, inducing an overall magnetic resonance that coexists with the individual electric resonance supported by each constituent nanoparticle. It has been shown that NCs support collective plasmon modes, and particularly induced electric and magnetic dipole resonances that can be tuned by varying the number of particles, their separation, and the background material permittivity [1]. As an effect of such collective dipole resonances, metamaterials made of close-packed ensembles of NCs exhibit resonant responses of the effective permittivity and permeability that can both reach negative values. If sufficient overlapping of the negative permittivity and negative permeability regions can be achieved by engineering the NC configuration, negative index in the optical range is realized.

NC metamaterials can be effectively fabricated by nanochemistry and self-assembly techniques. However, the fabrication of perfectly regular and exactly periodically arranged NCs is very far to be achieved with such bottom-up methods. In practice, there exist some disorder degrees at both the level of single constituent NCs and their assemblies, which can be not exactly periodical. It is therefore of interest to estimate the effect of such disorder on the optical properties of NC metamaterials. Moreover, self-assembling systems can be controlled to create specific periodic nanostructured patterns with long range order of the domains. However, the arrays of microdomains typically still contains some uncontrolled defects and usually lacks global registration and orientation. Accordingly, it is also important to characterize how these larger scale structural disorder effects are related to variations and degradation in the optical properties of NC metamaterials, and whether the electric and magnetic responses predicted for completely regular arrangements will be retained. The assignment of effective properties to such disordered metamaterials constitutes another challenging task.

In this work the optical response of disordered spherical NCs are studied by Monte Carlo simulations. Both the effect of dimensional and positional disorders in individual NCs are considered with the aim of selecting those structures which exhibit a significant magnetic response and are more stable with respect to irregularities. The impact of disorder on NC resonances is assessed by spectrally decomposing the scattered fields in terms of contributions of electromagnetic multipoles. Successive incorporation of the actual dipole moments into averaging procedures that do not require regular spatial arrangement can be used to characterize the effective permittivity and permeability of NC metamaterials.

II. MODELLING OF A DISORDERED NANOCLUSTER

A NC is formed by evenly distributing a number of colloidal metal nanoparticles around a central dielectric core, so as to obtain a compact and regular ensemble minimizing anisotropy and spatial dispersion effects. Depending on the number of constituent nanoparticles, their positions around the dielectric core can be assigned either analytically (regular NC), i.e., assuming that they coincide with the vertices of some Platonic solid, or by maximizing the minimum interparticle distance (pseudo-regular NC) [1]. Both these approaches provide theoretical distributions of nanoparticles that are substantially uniform, contributing to the desired isotropy of the NC optical response. The effect of disorder in nanoparticle sizes and positions are investigated separately. We introduce uncorrelated dimensional and positional disorder into the NC system by either adding to the nominal particle size random perturbations with uniform distribution over a given interval, or randomly displacing each nanoparticle within a spherical cap centered in its original position.

The approach outlined in [1] is applied to characterize the optical response of NCs. The single dipole approximation

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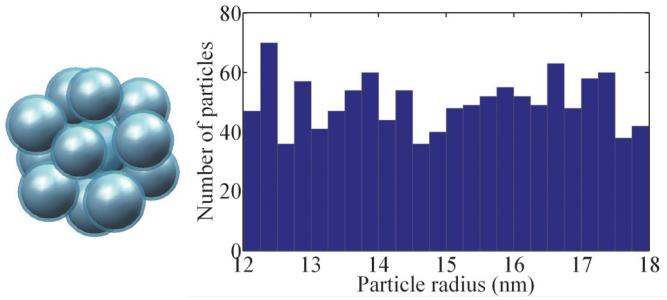
(SDA) [2] is used to determine the field scattered by a NC. The scattered field is then expanded into spherical harmonics and the various equivalent multipoles of the NCs are derived [3]. The frequency positions and strengths of NC resonances are identified through the analysis of the extinction, scattering, and absorption efficiencies.

The NC satellites are assumed to be made of silver, whose permittivity is described by the Drude model, where the various parameters are chosen to fit the measured permittivity of silver across the optical range [4]. To simplify the analysis, the host medium and dielectric core, as well as coating shells of nanospheres are supposed to have the same permittivity ($\varepsilon_r = 2.2$), which approximates the case of a glass core and NCs immersed in a solvent with similar permittivity.

III. Effects of Particle Size Disorder

NC dimensional disorder is modelled by assuming the size of each constituent nanoparticle to be a random variable with uniform distribution over the range $[r_0 - \Delta r_p, r_0 + \Delta r_p]$, where r_0 is the nominal particle size, and Δr_p is the considered maximum particle size variation. A population of NCs with random particle sizes is generated, and their individual scattering responses are calculated for illumination by a linearly polarized plane wave. Then, results for the scattering efficiencies are aggregated and the effect of dimensional disorder on the optical properties of NCs is characterized statistically (mean, variance, probability density function).

As an example, we refer to a regular icosahedral NC configuration made of 12 solid silver nanospheres of nominal radius $r_0 = 15$ nm, arranged around a central dielectric core of radius a = 18.2 nm, with overall NC size D = 116 nm. The surface-to-surface interparticle distance in the nominal configuration is set to 8 nm. We consider a maximum particle size variation $\Delta r_p = 3$ nm. Fig. 1(a) shows one of the NC from the generated population of 100 samples with random particle sizes. The histogram plotted in Fig. 1(b) confirms that particle size distribution is substantially uniform over the considered size range. After simulation by the SDA and multipole expansion of the scattered fields for each NC of the population, results for the dipolar and higher order multipole scattering efficiencies are aggregated into the statistics shown in Fig. 2. To comprehensively characterize fluctuations in the strengths and positions of NC resonances induced by the variability of particle size, in Fig. 2 we have plotted the 5th, 50th, and 95th percentile curves along with the corresponding empirical probability density functions (grey shaded stripes behind plotted curves). Solid lines represent the reference scattering efficiencies for the nominal icosahedral NC configuration. All NC collective resonances are slightly detuned with respect to the nominal NC resonance frequencies. The variances of the scattering efficiencies are proportional to the width of grey stripes or, equivalently, to the inter-percentile range. In particular, the spread of the magnetic dipole scattering efficiency is larger than that of the electric dipole scattering efficiency, likely due to the fact that the magnetic resonance depends both on the size of the equivalent loop formed by currents circulating around the NC central dielectric core and the dimensions of individual particles forming this loop, whereas the electric dipole resonance mainly depends on these latter. Analogously, the magnetic dipole resonance strength is reduced more noticeably than that of the electric dipole.



(a) (b)

Figure 1. (a) Sample icosahedral NC with random particle sizes ($r_0 = 15$, $\Delta r_p = 3$ nm). (b) Particle size distribution for the considered population of 100 NCs.

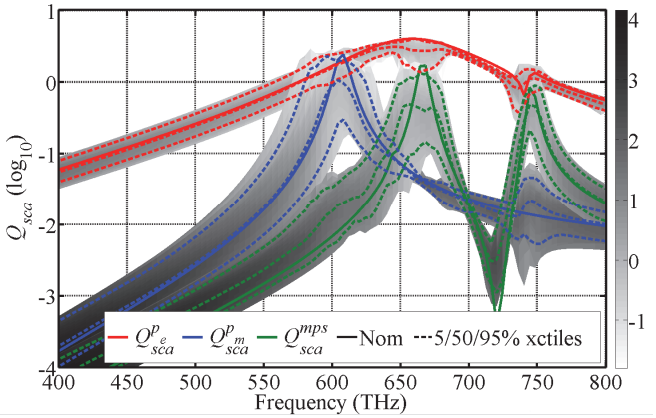


Figure 2. Statistics of the scattering efficiencies associated with the induced electric and magnetic dipoles and the remaining higher order multipoles for a population of 100 icosahedral NCs with $r_0 = 15$ nm and for $\Delta r_p = 3$ nm.

Acknowledgement

The authors acknowledge partial support from the European Commission 7th Framework Program FP7/2008, "Nano-sciences, Nanotechnologies, Materials and New Production Technologies (NMP)" theme, research area "NMP-2008-2.2-2 Nanostructured meta-materials", grant agreement no. 228762.

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