Plasmonic nanoparticles assemblies: Preparation, structure and optical properties.

T. Bürgi* and A. Cunningham

*Presenting author

Département de Chimie Physique, Université de Genève
Quai Ernest-Ansermet 30, CH-1211 Genève 4
Fax: +41(0)22 379 61 03; email: thomas.buergi@unige.ch

Abstract

Strategies to assemble plasmonic particles into larger entities are described. These include the use of surfactants leading to hierarchical organization of metal particles, the build-up of layered structures on flat substrates using polyelectrolytes and the fabrication of core-shell systems. The optical properties have been characterized and compared with simulations of the corresponding model systems.

1. Introduction

Our goal is the preparation of metamaterials in the visible spectral range using self-assembly routes. Such an approach is based on the coupling of plasmons of individual nanoparticles within larger structures. Concepts like the meta-metamaterial [1] or the core-shell system [2] have been proposed and it has been demonstrated theoretically that the scattering response of a cluster of metallic nanoparticles sustains a strong magnetic dipole moment. Forming a sphere out of such a material allows observing a strong Mie resonance associated with a magnetic dipole [3]. The amorphous arrangement of such spherical clusters in space would induce dispersion in an isotropic effective permeability.

We report on our experimental attempts for the realization of such structures using different strategies involving the use of surfactants to form nanoparticle composites or the use of dielectric beads and the assembly of metal nanoparticles at its surface (core-shell structures). We furthermore fabricated systems where nanoparticles were assembled in arrays on a flat substrate by a layer-by-layer deposition using poly-electrolytes in order to exploit coupling between particles in different arrays. The experimentally determined structure and optical response of the assemblies were used to derive adequate model systems that allowed the simulation of the spectral response and extraction of optical properties.

2. Nanoparticle-surfactant composite materials

Gold nanoparticles of various sizes (17nm and 40 nm) were organized within a nanoparticle – surfactant composite [4]. The latter was fabricated in a two-step procedure. First the gold nanoparticles were prepared using the Turkevich-Frens method [5]. In a second step a thiol surfactant, EGMUDE (triethyleneglycolmono-11-mercaptoundecylether) was added in excess to the aqueous nanoparticle solution. Extinction spectra spectra showed a strongly red-shifted plasmon resonance (Figure 1) and dynamic light scattering revealed the formation of larger assemblies of gold nanoparticles, which was then also confirmed by transmission electron microscopy (TEM, see Figure 1). These entities represent hierarchical structures composed of gold nanoparticles clustered together into larger aggregates of about one μm. Several of these entities again cluster together to even larger units. These structures strongly resemble the meta-metamaterials proposed earlier [1]. The assembly of the nanoparticles is guided by the EGMUDE, which also stabilizes the particles. Current experimental challenges with these materials is their limited stability.

In order to better understand the optical response calculations were performed on analogous structures by applying analytical solutions of Maxwell's equations for particles with a spherical symmetry, known as Mie-theory, which was extended to handle aggregates of spheres. With this method one can calculate all quantities of interest for clusters consisting of arbitrarily arranged nanoparticles with a spherical shape. Such calculations very well reproduced the shifted plasmon resonance and furthermore indicated that the dominating contribution to this spectral feature arises from a magnetic dipole oscillation that is induced due to the spherical shape of the fabricated supramolecular clusters. A dispersive behavior in the effective permeability was furthermore revealed, as can be seen in Figure 1 (right). Calculations will in the future guide the material design for optimizing the dispersion in the effective permeability.
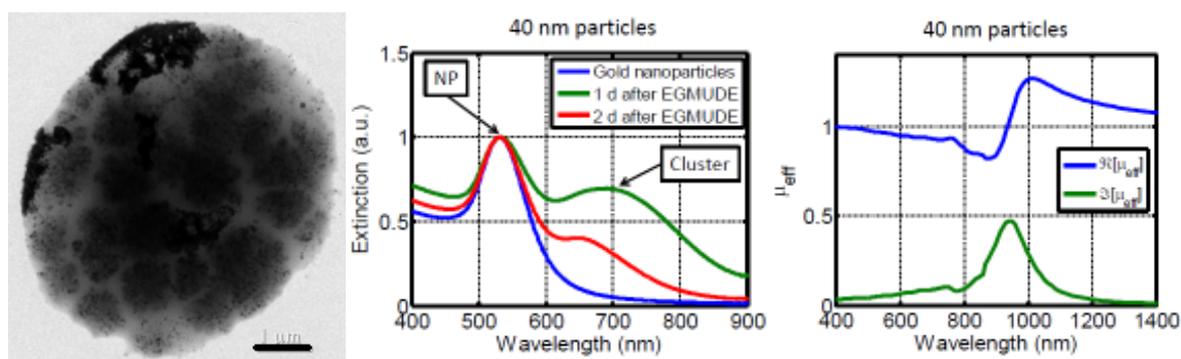
Figure 1: Gold nanoparticle surfactant (EGMUDE) composite material. Left: TEM micrograph (scale bar corresponds to 1 μm); middle: Extinction spectra; right: Simulated effective permeability for model clusters.

3. Layered nanoparticle arrays

Gold nanoparticle arrays (Figure 2) were prepared on glass substrates using layer-by-layer self-assembly by first depositing negatively charged gold nanoparticles on a positively charged substrate. On top of that first gold nanoparticle layer polyelectrolyte multilayers were adsorbed followed by a second gold nanoparticle array.
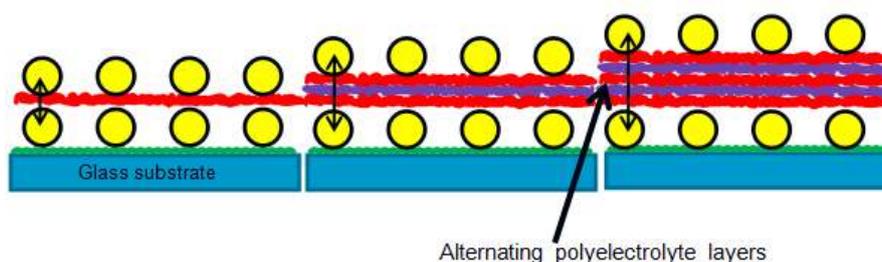
Figure 2: Schematic of nanoparticle – polyelectrolyte multilayer system.

The change observed in the spectral profile of the layer upon the introduction of a second nanoparticle array depends upon the size of the nanoparticles, their separation, and the polarization and direction of the incoming radiation. The necessary control of spacing can be achieved through the build-up of individual polyelectrolyte (PE) layers in-between the gold nanoparticle arrays in an extensively studied process known as layer-by-layer assembly [6]. Here, the separation between the arrays of gold nanoparticles depends solely on the number of polymer layers used. The electrostatic attraction between the oppositely charged polymers and the introduction of negatively charged gold NPs gives rise to a highly flexible system with a large degree of control over a wide variety of parameters, almost to within nanometer precision.

Grazing Incidence Small Angle X-ray Scattering (GISAXS) studies were performed to study the structure of the gold nanoparticle bilayers (Figure 3). From such measurements the relevant distances between particles and layers were extracted. The results agreed well with the structure determined from the SEM images.
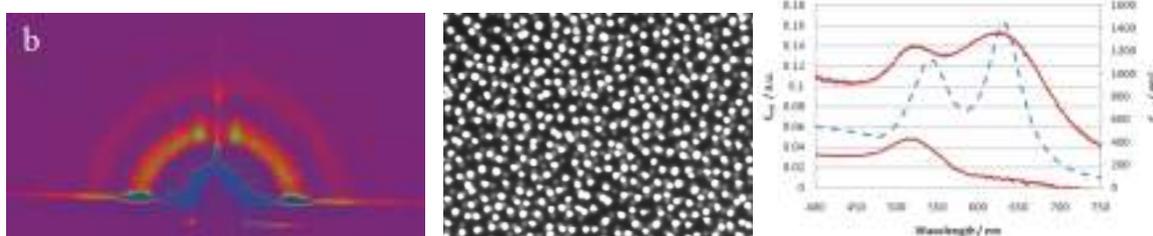
Figure 3: GISAXS pattern (left) and SEM (middle) of a gold nanoparticle bilayer separated by 11 (left) and 31 (right) polymer layers. The bright and faint spots in the SEM correspond to nanoparticles in the top and bottom layer, respectively. Right: Experimental (red) extinction spectra of single (bottom) and double gold nanoparticle array (top). The simulated spectrum (dashed blue) based on a nanoparticle dimer model is in good agreement with experiment.

Within one nanoparticle layer the separation is quite large such that intra-layer plasmon coupling is small. However, coupling between particles within different layers is significant. Based on this structural feature simulations were performed on nanoparticle dimers [7]. These simulations were done within the framework of Mie theory, which is extendable to layers of periodically arranged spheres[8] or to an arbitrary arrangement of spherical particles [9]. At short layer separations plasmon hybridization was seen to occur with the splitting of the dipolar excitation observed in single gold nanoparticles into two separate resonances – the longitudinal σ and transversal π^* modes, in good agreement with the simulations (see Figure 3).

4. Conclusions

Using physical chemical self assembly principles it is possible to organize metallic nanoparticles that sustain plasmon resonances. The assembly leads to plasmon coupling within the larger structures. Three-dimensional and core-shell structures as well as layered array structures were prepared, their structure determined and their optical response compared to simulations. It is this interplay between theory and experiments that we will use in the future to guide the rational design of metamaterials in the visible spectral range.

References

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