3-dimensional arrays of plasmonic nanospheres fabricated by Langmuir-Blodgett technique

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Abstract

In this paper we present a self-assembly technique that enables the fabrication of dense 3-dimensional lattices of plasmonic nanoparticles of sizes significantly shorter than the wavelength of visible light (i.e. lower than 100 nm). Compact monolayers of nanoparticles are first formed at the surface of water (Langmuir films) and transferred on to appropriate substrates (Langmuir-Blodgett layers). Bulk 3D materials are obtained over large areas (typically square centimetres) by successive transfer of identical monolayers. The distance between the metallic nanoparticles is accurately controlled by the thickness of a dielectric shall surrounding them. The quality of the final material is evidenced by scanning electron microscopy. It depends strongly on the surface chemistry of the nanoparticles. Some optical properties of the fabricated materials are reported.

1. Introduction

The creation of bulk metamaterials operating at visible light frequencies is constrained by two strong requirements namely (i) the fabrication of artificial nanosized resonators that generate the local extraordinary electromagnetic response and (ii) the dense assembly of these resonators in three-dimensional arrays with sub-wavelength unit cells. The concept of effective electromagnetic parameter requires that the typical sizes a of the local nanoresonators should be much shorter than the wavelength λ of visible light (e.g. $a \sim \lambda/10$ yields $30 < a < 80$ nm). Fortunately, gold or silver nanoparticles can be used as plasmonic nanoresonators and nanochemistry offers the possibility to synthesize large amounts of them with the required sizes. Moreover, the distance between the plasmonic resonators can be easily controlled if the particles are designed as core – shell objects in which the metallic core is surrounded by a dielectric shell of well defined thickness.

Fig 1: Schematic view of a regular assembly of core-shell nanoparticles. The metal cores are separated by twice the thickness of the dielectric shell (Silica).

These basic requirements mean that the fabrication of a bulk sample involves the assembly of more than 10^{12} nanoresonators per cubic millimetre! Self assembly hence appears as the only realistic way to assemble such a huge number of objects. Ideally, self assembly of 3-dimensionally ordered lattices

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occurs spontaneously under the simple action of the pair interaction between particles. The narrowness of the size distribution and the chemical control of the surface function are then two crucial parameters for a perfect ordering of the nanostructure. The combination of colloidal forces that govern the pair interaction is actually quite complex and examples of perfect ordering of nanosized particles are spectacular but rare [1].

In this work, we have chosen a hybrid (or semi-directed) method in which self-assembled monolayers are stacked one by one to construct a 3-dimensional material.

2. Langmuir-Blodgett technique and surface chemistry of sub-wavelength nanoparticles:

The Langmuir-Blodgett (LB) method has been extensively used to construct multilayers of amphiphilic molecules (surfactants) or nanoobjects [2]. It consists of three main steps namely: (i) spreading of the nanoobjects at the surface of water (ii) compression of the surface layer by a mobile barrier in order to form a compact monolayer (so-called Langmuir film) and (iii) transfer of the film onto a solid substrate slowly pulled out across the water surface. Repeating the process N times results in a material with controllable thickness (N layers).

The advantage of this method is that it enables the fabrication of homogeneous materials over large lateral dimensions (up to centimetres). The thickness of the stack is in principle not limited: numbers of layers N as high 100 have been reported [3]. In most cases, applications were in the domain of photonic crystals and the sizes of the particles exceeded 200 nm. It turns out that assembling smaller particles gets more and more difficult as the sizes are reduced and we had to revisit the surface chemistry to scale down the sizes.

Since the targeted NPs have a core-shell structure with a silica shell, we decided to optimize first the surface chemistry of plain silica NPs (cheap and easy to synthesize) and transfer the optimized functionalization protocol to the active core-shell NPs. Our strategy was to decrease progressively the size of the NPs from ~ 200nm to the desired sizes of a few tens of nm.

Large quantities of monodisperse silica NPs are synthesized by the classical Stöber method in aqueous solvent. The surface of the NPs is modified by subsequent grafting of amino-propyl-trimethoxy-silane, hence making the NPs more hydrophobic and dispersable in chloroform.

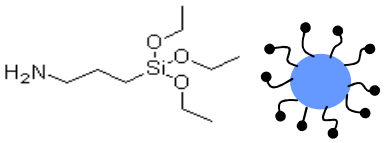

Fig. 2: Sketch of the surface modification of the NPs by addition of an amino-propyl-trimethoxy-silane. The particles are subsequently dispersed in chloroform.

3. Structure of the fabricated materials: 2d monolayers and 3d materials

The NPs were then deposited on water on the Langmuir trough (model KSV Minitrough) and transferred on hydrophilic substrates (glass or silicon). The control parameter are (i) the concentration of the grafted amino-silane, (ii) the surface pressure during transfer, (iii) the speed of transfer and (iv) the time constant of the feedback loop that controls the surface pressure of the Langmuir trough (in commercial KSV software).

Figure 3 below shows the organization of monolayers deposited on glass substrates. The layers are dense and uniform over wide areas (typically square centimetres). The transfer of several successive monolayers has been successfully achieved with no loss of quality. The smallest size of 90 nm is significantly lower than the wavelength of visible light.

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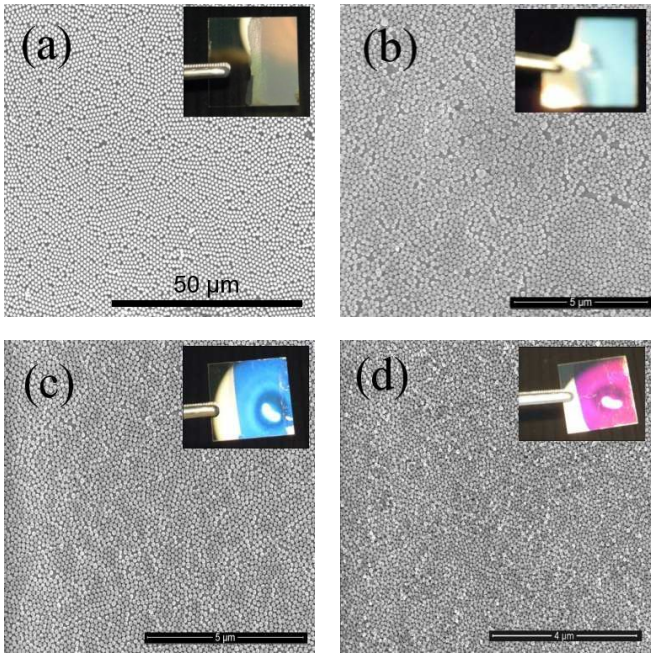

Fig. 3:
SEM micrographs of monolayers of silica nanoparticles transferred on a glass substrate by the Langmuir-Blodgett technique. The diameter of the NPs is progressively reduced from (a) 1µm to (b) 175 nm, (c) 140 nm and (d) 90 nm. Inset shows a photograph of the substrate (18x18mm² glass plate) after transfer. The reflected color of the deposited layer looks perfectly uniform over centimeter scale.

Finally, core-shell nanoparticles (silver core-silica shell) of the same external size (~ 100 nm) have been assembled and the first optical measurements performed on these materials will be reported.

4. Conclusion

We have assembled dense regular 3 dimensional arrays of plasmonic nanoparticles by the Langmuir-Blodgett technique. We believe that these new materials are good candidates for the observation of meta-properties such as extraordinary values of the dielectric permittivity.

References

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