Self-assembled nanostructured metamaterials for applications in visible light

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Abstract

In this paper we present the fabrication of nanostructured metal-dielectric composite materials that are designed to exhibit dielectric resonances at visible light frequencies. The resonators are constituted of silver and gold nanoparticles coated with a dielectric silica shell that enables a fine tuning of the distance between the plasmonic cores. These core-shell nanoresonators are self-assembled in close-packed monolayers and transferred onto a solid substrate by a Langmuir-Schaefer method. Three dimensional materials of controlled thickness are then obtained over large areas. The electromagnetic behaviour is investigated by reflectance experiments at normal incidence. The presence of strong dielectric resonances is demonstrated and the variations of the effective refractive index vs. wavelength are inferred.

1. Introduction

The fabrication of bulk metamaterials operating in visible light appears as a fantastic but difficult challenge for future applications. The top-down approaches based on lithography techniques have been very successful in producing nanostructured meta-surfaces. However, they are not well adapted to the fabrication of three dimensional structures. Moreover, bulk samples require the fabrication and the assembly of a huge number of nanosized resonators (of order 10^{12} or more per mm^3). Self assembly is often cited as the only realistic way to achieve this goal.

In this paper, we describe a fabrication route combining nanochemistry and self-assembly for the fabrication of three-dimensional nanostructured metamaterials. The meta-atoms consist of metallic nanoparticles (silver or gold) coated by a dielectric shell of silica. The metallic cores generate localized surface Plasmon polariton resonances (LSPR) in the visible light domain whereas the silica shell fixes a constant distance between the cores. These core-shell plasmonic resonators are self-assembled in Langmuir monolayers at the surface of water and transferred onto solid substrate via an adapted Langmuir-Shaefer method to build a close-packed three dimensional stack. This method enables a fine tuning of the distance between the metallic cores by adjusting the thickness of the silica core and the fabrication of homogeneous samples of large area and controllable thickness.

The electromagnetic response of the fabricated materials is linked to the presence of dielectric resonances. Unusually large and low values of the real part of the effective refractive index are expected.

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2. Fabrication of the nanostructured metamaterials:

<u>Synthesis of the core-shell Ag@SiO2 nanoresonators:</u>

This synthesis is done in two steps: silver nanoparticles of 27 nm are first synthesized and dispersed in absolute ethanol following a method derived from Zhang et al. [1]. A silica shell is then grown from hydrolysis/condensation of a TEOS precursor catalyzed by ammonia in alcoholic medium [2]. The obtained particles are characterized by transmission electron microscopy (TEM) and UV-VIS-NIR spectroscopy (Figure 1).

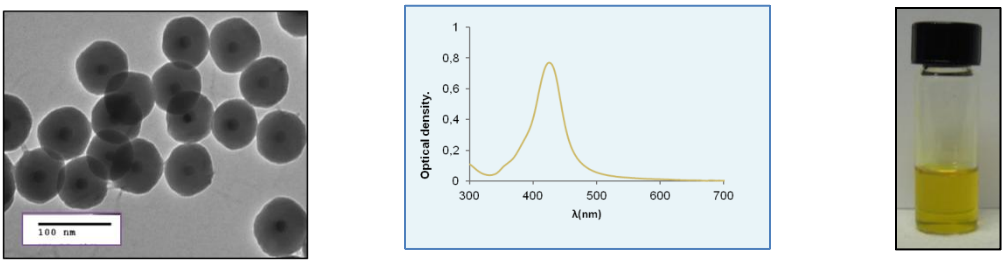

Fig. 1: Left: TEM view of the core-shell AgSiO2 nanoresonators. Centre: Optical density in the UV-Visible spectrum showing the Plasmon band at 429 nm. Right: picture of the solution.

<u>Multilayer assembly:</u>

After synthesis, the hydrophilic surface of the nanoparticles is modified by grafting an aminopropyl-triethoxysilane [4] to enable dissolution in an organic solvent and formation of stable monolayers on water. The Langmuir monolayers are prepared the usual way: a solution of nanoparticles is slowly deposited on the water surface of a KSV Minitrough Langmuir trough. After complete evaporation of the organic solvent, the surface layer is slowly compressed by reducing the trough area until a dense monolayer is obtained. The self-assembled monolayers are then transferred onto an immersed silicon wafer by lowering the water level (Langmuir-Shaefer method). Multiple layers are obtained by repeating the transfer process. Figure 2 shows high resolution SEM micrographs of the obtained materials.

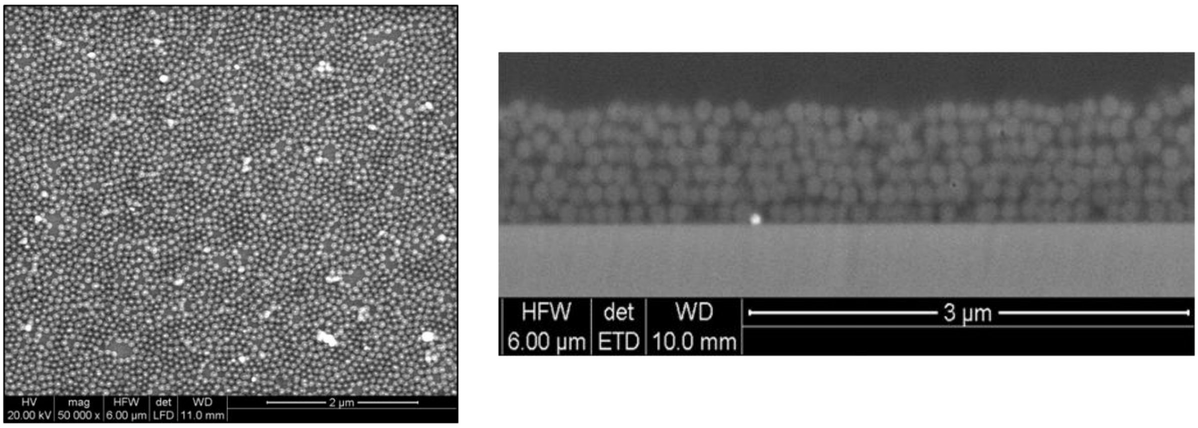

Fig. 2: Left: top view of a layer of Ag@SiO2 core-shell nanoparticles deposited on a silicon substrate obtained by high resolution scanning electron microscopy (SEM). Right: side view of a 6-layers stack.

3. Optical reflectance:

In order to characterize the optical properties of the materials, optical reflectance experiments were carried out at normal incidence with a UV-Visible-NIR Micro-spectrophotometer from CRAIC Technologies on several sets of samples.

Figure 3 shows a typical plot of the reflected intensity vs. wavelength for a sample made of 7 layers of Ag@SiO2 particles. A plasmon band is observed around 400 nm in addition to a classical system of Fabry-Perot fringes. The data are successfully reproduced by a simple phenomenological model based on a single Lorentzian resonator. As a result, the variations of the refractive index are obtained vs. wavelength and sample thickness.

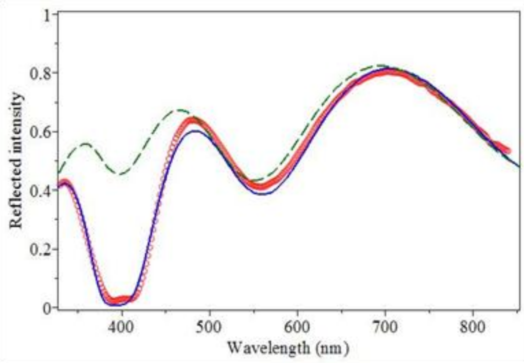

Fig. 3: Intensity reflected at normal incidence on a sample made of 7 layers of core-shell Ag@SiO2 nanoparticles. Data points are shown in red. The solid line in blue is a fit to the phenomenological model. The dashed green line show the Fabry-Perot fringes calculated for silica spheres in absence of Ag resonator.

This study shows that:

(i) The refractive index of the composite material is strongly modulated in the vicinity of the LSPR.

(ii) The EM behaviour is well reproduced by a phenomenological model assuming a single Lorentz resonator whereas simple homogenization models fail.

The variation of the resonance frequency with thickness and the crossover from 2D to 3D behaviour are presented.

The technique has been extended to Ag@SiO2 composites with higher volume fraction of silver and to gold@silica composites.

4. Conclusion

This study shows that the association of nanochemistry and self-assembly enables the fabrication of nanostructured metamaterials operating in visible light. It opens the way to the fabrication of low-index materials. The authors acknowledge support from the FP7 Collaborative project METACHEM under grant # 228762.

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