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Silver nanorings metasurface for enhanced absorption at optical frequencies

I. Bouanane *[ab], J. Le Rouzo[a], O. Margeat[c], A. Capitaine[c], B. Sciacca[c], G. Berginc[c], L. Escoubas[a],
[a]Institut Matériaux Microélectronique Nanosciences de Provence, Aix-Marseille Univ., CNRS (France), Univ. de Toulon (France); [b]Thales LAS France SAS (France); [c]Aix Marseille Univ, CNRS, CINAM, Marseille, France.

ABSTRACT

Plasmonic nanoparticles are key to the realization of selective light absorbers, and especially metallic nanoparticles that exhibit tunable optical properties with implications in multiple fields such as photovoltaic, photodetectors and optical filters [1]. Among those nanoparticles, metallic split-ring resonators are metamaterials with optically induced magnetic responses allowing unique possibilities for controlling light and enhance absorption in the visible and near IR domains depending on their geometric parameters.

The objective of this research is to show the enhancement of absorption at optical frequencies by not only designing a metasurface made of silver split-rings with realistic geometric parameters but also providing a first proof of concept of those tunable circular nanorings entirely made by scalable bottom-up approaches.

First, Finite Difference Time Domain (FDTD) simulations were performed to optimize the silver nanoring geometric properties thanks to a parametric study (inner, outer diameters, thickness, split-ring gap, array periodicity). This showed full control on resonance peaks and absorbance enhancement in the visible and near IR.

Next, we showed the realization of circular silver split-ring arrays on a large area via bottom-up techniques. Silver single-crystalline nanocubes (synthesized in solution via the polyol process) were self-assembled in Polydimethylsiloxane (PDMS) templates previously nanostructured with a pre-defined split-ring motif. Epitaxial nanowelding techniques at low temperature [2] were then employed to connect the individual nanocubes together to obtain a continuous quasi-monocrystalline material.

Keywords: Metasurface, nanorings, split-ring resonators, bottom-up technique,

1. INTRODUCTION

The design of absorbent metasurfaces in the visible and infrared ranges is key in various application fields such as solar photovoltaic and solar thermal, optoelectronics (photo-detectors, sensors, etc.) or even functionalized materials (selective absorbers). For this, the opportunity to use nanostructures of size well below the wavelength to control the light-matter interaction has aroused considerable interest during the last decade, thanks in particular to the unique optical properties that can be obtained with metamaterials or metasurfaces.

Previous research work carried out, in particular by the IM2NP laboratory and Thales [3], has shown that it is possible to design absorbent materials in the form of synthesized and deposited metasurfaces, composed of metal nanoparticles of different shapes, sizes and nature included in a transparent polymer matrix. These easy-to-use metasurfaces exhibit very interesting absorption properties in the visible domain. Until then, only the electrical part of the electromagnetic field of metallic nanoparticles was considered in most studies mentioning an experimental proof of concept in the visible. Regarding the magnetic component of the electromagnetic field, the absorption frequency bands of systems composed of naturally magnetic nanoparticles, are limited to the Gigahertz range as shown for example by studies on absorbers based on iron nanoparticles of 1 nm size which have a maximum absorption frequency of 130 GHz [4]. However, there are different approaches in the literature overcoming these limitations and providing a magnetic response to optical waves thanks to artificial optical materials, in particular metamaterials with negative permeability or negative refractive index [5-8].

A new area of study therefore concerns the response of nanostructures to the electrical and magnetic components of light in visible and infrared frequencies. The design of a metasurface composed of nanomaterials could allow the optical response of these nanostructures to be controlled and optimized very precisely in the bands of interest. For this, the well-known pattern of split ring resonators is used here to achieve a first proof of concept of an optical absorber in the visible and IR bands (Near Infrared (Near IR) and Short-Wave Infrared (SWIR)). Metal split-ring resonators are metamaterials with optically-induced magnetic responses thanks to their circular shape. They exhibit resonant magnetic response in addition to their resonant electric response. Using split-ring resonators therefore allows to expect the electric and magnetic fields to be enhanced when resonance occurs and consequently to cause an enhancement of absorption properties at the resonance wavelength. In addition, split-ring resonators allow unique possibilities for precisely controlling the light response depending on their geometric parameters. Moreover, more than creating a simple absorbent metasurface, the objective is to create an absorbent artificial skin allowing easy deposition, that will be flexible and can be laid out on any surface.

The goal of this study is therefore to propose a first proof of concept thanks to the realization and characterization of a tunable absorbent metasurface composed of silver nanorings whose optical absorption properties will be optimized in the visible and near infrared domains. A first theoretical simulation approach is thus carried out in order to predict the optical properties of the structure and to optimize them before its experimental realization. Then, this artificial skin has been entirely made by scalable bottom-up approaches which potentially allows a large-scale realization.

2. FDTD SIMULATION

2.1 Simulation tools and simulated system

Prior to the realization of the absorbent metasurface, simulation work was carried out in order to study the optical response of the structure and to optimize it. The numerical simulations were performed using an FDTD (Finite Difference Time Domain) calculation method under the commercially available software Lumerical [9] allowing simulation of the light interaction of particles of various shapes.

The optical properties such as the absorption and scattering cross sections are computed for one, two and four silver nanorings in vacuum. The use of a total-field scattered-field source (TFSF), as illustrated in Fig. 1, allows the computation region to be separated into two distinct regions: a total field region which includes the sum of the incident field wave as well as the scattered field and the scattered field region which includes only the scattered field. This source makes possible to study small nanostructures illuminated by a plane wave. An absorption monitor is located inside the TFSF source. It measures the net power P flowing through the particle and, normalizing it to the intensity of the source I, returns the absorption cross section σ_{abs}. The scattering cross section σ_{sca}, which is the power P divided by the power by unit of area of the incident beam I, is calculated by a monitor placed outside the source region.

$$\sigma_{abs\ (sca)} = \frac{P_{abs\ (sca)}}{I} \tag{1}$$

The extinction cross section σ_{ext}, which is the measure of the attenuation of the light traversing the nanoparticle from which the energy is removed by scattering and absorption, is then calculated. Finally, to remove the size dependence and to compare the optical responses of the various nanostructures, the extinction efficiency Q_{ext} is calculated by the relation:

$$Q_{ext} = \frac{\sigma_{abs} + \sigma_{sca}}{A} \qquad (2)$$

where A is the area of one nanoring.

In the calculations, a plane-wave of light is normally incident along the z-axis and the electric field is x-polarized. Perfect Match Layer (PML) boundary conditions were used in all the directions. The optical constants for silver are extracted from Johnson & Christie's experimental data [10].

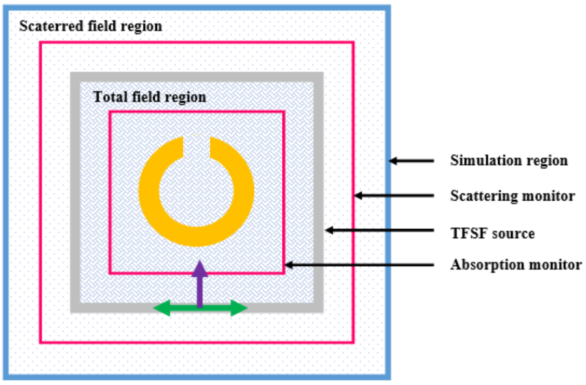

Figure 1: FDTD calculation region

First, a parametric study was performed to define the geometric parameters of individual nano-objects to optimize electromagnetic performance in the wavelength band of interest. For this, the scattering and absorption spectra of the individual nanorings were obtained. Their frequency of resonances were determined according to their geometric parameters which are the inner and outer radii of the silver nanoring, 'h_1' and 'h_2' respectively, the thickness of the ring 'z' and the split-ring gap 'g', as shown in the figure 2. Once this study was carried out, the geometric parameters of a single silver nanoring were defined in order to satisfy both the absorption at the wavelength of interest of 1500 nm together with realistic parameters suitable for realization. Then, the periodicity factor of the system could be studied in the x axis with a couple of particles before studying it in the x and y axes with 4 particles together in vacuum.

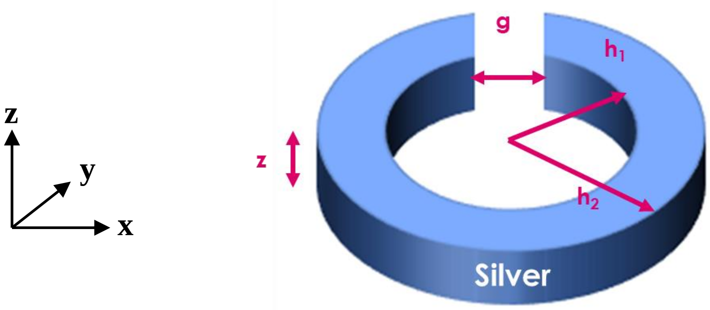

Figure 2 : Schematic of the silver nanoring structure. The inner radius of the ring is labeled 'h_1', the outer radius 'h_2', the thickness 'z' and the split-ring gap 'g'.

2.2 Simulation results

The parametric study carried out on an individual silver nanoring to predict its optical response showed that the more the inner radius h_1 increases, the more the extinction efficiency Q_{ext} peak shifts towards IR and the more the scattering and absorption efficiencies increase. The more the outer radius h_2 increases, the more the extinction efficiency Q_{ext} peak widens and shifts towards IR and the more the scattering and absorption efficiencies decrease. Regarding the thickness z and the split-ring gap, the more they increase the more the extinction efficiency Q_{ext} peak shifts slightly towards visible. The most important fact noticed by this parametric study is that the more the split-ring gap g increases, the more the scattering efficiency decreases but, above all, the more the absorbing efficiency increases, while shifting the absorption band as shown in the figure 3 with a silver nanoring which has an inner radius of 30 nm, an outer radius of 60 nm and a thickness of 30 nm.

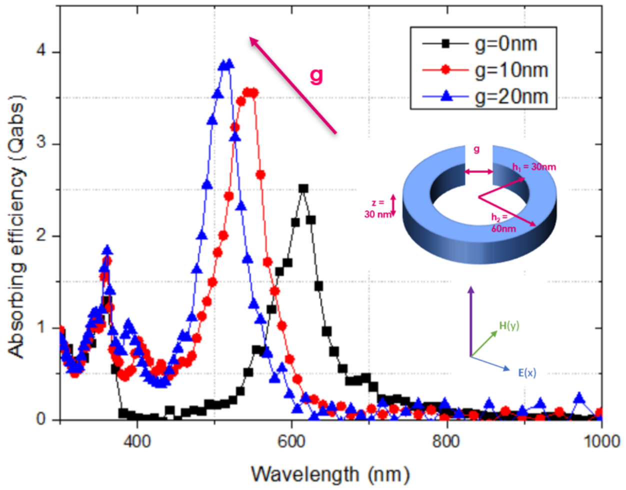

Figure 3 : Wavelength-dependent absorbing efficiency of the structure shown (h1 = 30nm, h2 = 60nm, z=30 nm), the split-ring gap being varied.

The results of this parametric study have allowed to define a set of parameters of a silver nanoring, suitable for realization and showing enhancement of the absorption properties at a wavelength of 1500 nm as shown in the figure 4. Indeed, the pattern that will make up the metasurface and whose periodicity will be studied below, has an inner radius of 250 nm, an outer radius of 305 nm, a thickness of 30 nm and a split-ring gap of 100 nm.

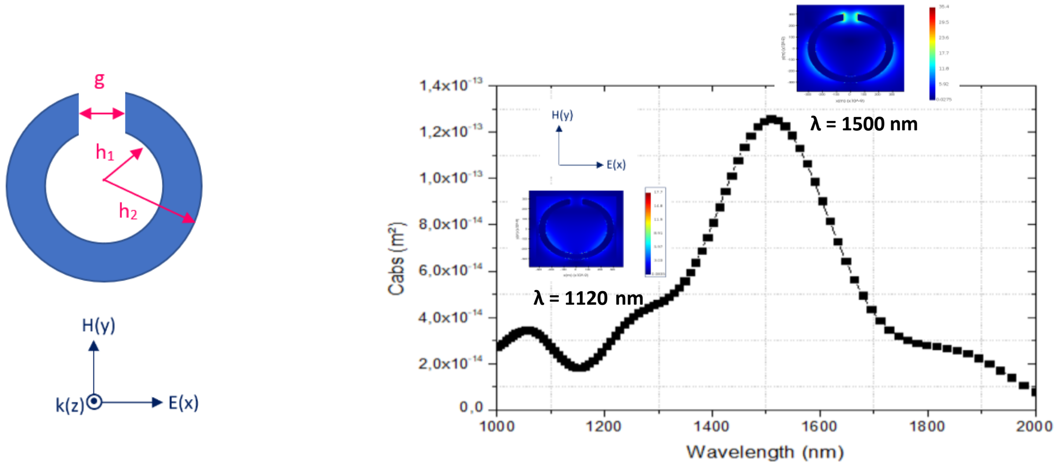

Figure 4 : a) Structure of silver nanoring showing a resonance peak at 1500 nm.

b) Wavelength-dependent absorbing efficiency of the structure a)

Once the parameters of the individual ring allowing absorption at the wavelength of interest of 1500 nm were defined, the periodicity of the pattern was studied with these same nanorings parameters. First, by studying the optical response of a couple of nanorings with the objective to see how the free-space distance impacts in the x-axis (d). The figure 5 shows an exaltation of the absorption properties at 1500 nm for two nanorings spaced by 390 nm, compared to the response of one single nanoring. Then, the optical properties of four nanorings were studied in order to see the impact of the free-space distance in the x-axis (d) but also in the y-axis (p). The figure 6 shows a great exaltation of the absorption cross section (more than three times greater) at 1500 nm for four silver nanorings spaced by 390 nm in the x and y axes, compared to one single nanoring. Consequently, the motif chosen to be realized is therefore an array of silver nanorings, each having an inner radius h_1 of 250nm, an outer radius h_2 of 305 nm, a thickness z of 30 nm, a split-ring gap g of 100 nm and being spaced from each other by 390 nm. The comparison of the absorbing cross section of a single, two and four nanorings suggests, indeed, even more exalted absorption properties with an ordered array of nanorings, as shown in the figure 7, and justifies the interest of realizing this metasurface motif.

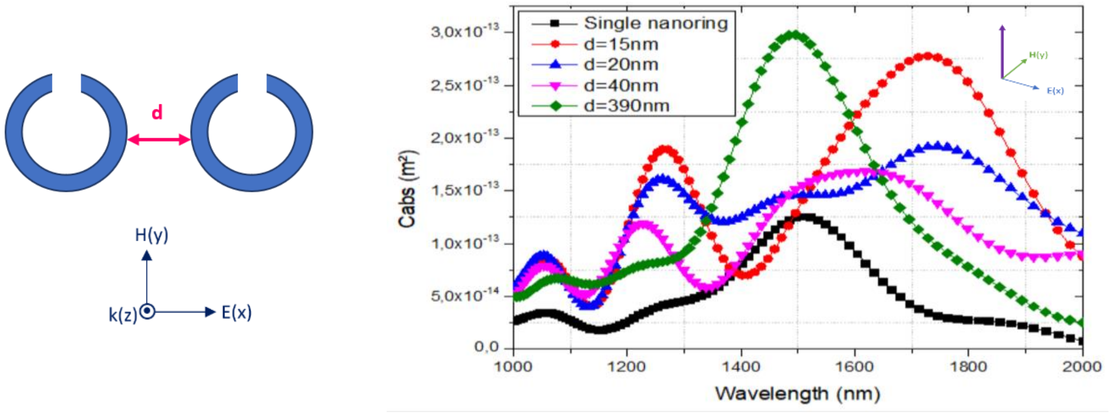

Figure 5 : Wavelength-dependent absorption cross section of a couple of nanorings with the free space distance d being varied in the x axis. The structure of the single nanoring is shown in Fig. 4 a).

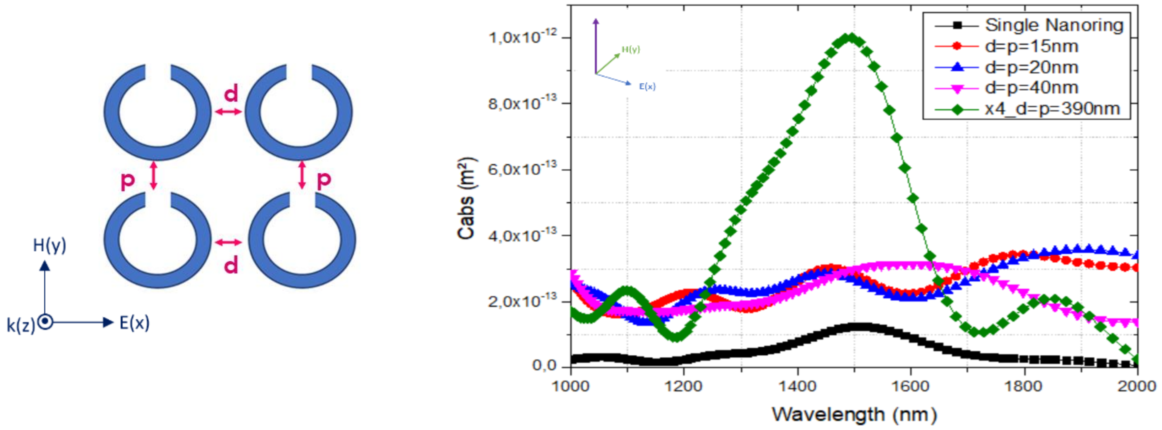

Figure 6 : Wavelength-dependent absorption cross section of four silver nanorings with the free space distances, d being varied in the x axis and p being varied in the y axis. The structure of the single nanoring used is shown in Fig. 4 a).

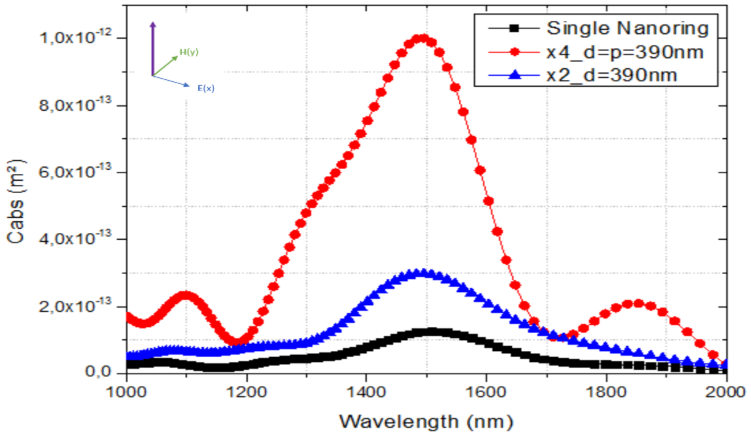

Figure 7 : Wavelength-dependent absorption cross section of a single nanoring in black, two nanoring spaced by 390 nm in the x axis in blue and four nanorings with a free space distance of 390 nm in the x and y axes in red. The parameters of the single nanoring used is shown in Fig. 4 a).

3. BOTTOM-UP REALIZATION

The performed numerical simulations allowed to define a set of parameters in order to realize the metasurface by a bottom-up technique allowing large scale realization. Indeed, the artificial skin is made by an assembly of silver nanocubes, whose we know perfectly well how to control their size, that are deposited on a PDMS substrate. The choice of this polymer allows to meet the objective of an absorbent artificial skin which can be placed on any surfaces. Indeed, the PDMS can be flexible and is transparent and non-absorbent in the frequency range of interest. The nanocubes will therefore be deposited in a PDMS mold forming the pattern defined by the numerical simulations with the objective of creating nanorings in a continuous material. The different realization steps will be detailed below.

The first step consists of the colloidal synthesis of silver nanocubes in the size of interest. The synthesis follows a polyol process, developed by Qiang Zhang et al [11], and enables the generation of silver nanocubes, in large quantity, of monodisperse size and shape in a reproducible manner. This synthesis allows an accurate control of the growth stages and consequently the morphology of the nanoparticles, producing nanocubes with edge between 30 and 70 nm depending on the reaction time. The nanocubes stored in distilled water remain stable for several months [12].

In the meantime, a silicon master is realized following the classical process of electronic lithography and etching, as illustrated in the figure 8. This master, that could be reused as many times as necessary, is the negative of the PDMS mold where the assembly of the nanocubes is then realized.

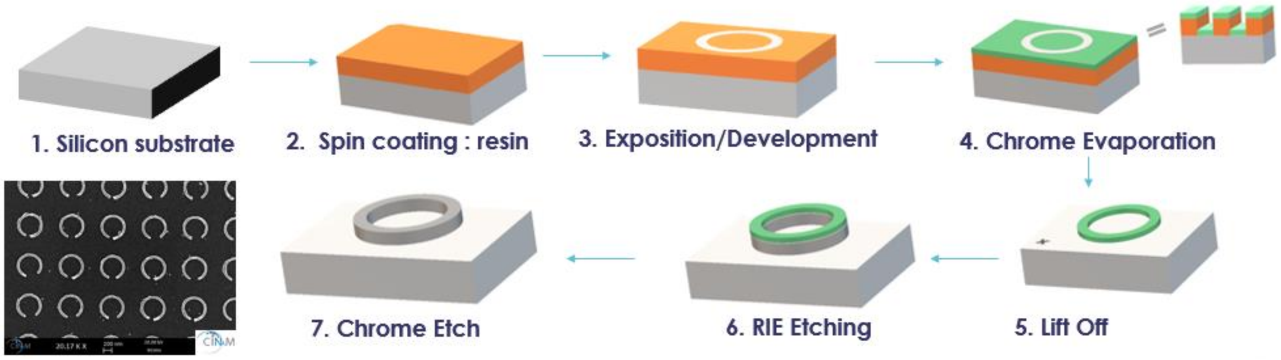

Figure 8: Silicon master realization process by electronic lithography and RIE etching

For that, the PDMS template is obtained, after demolding, by cross linking of the PDMS deposited on the silicon master. A capillarity process is then carried out for depositing the colloidal nanocubes within the PDMS template, which thus form the desired pattern. We acknowledge that the nanocubes are deposited side by side to form the nanoring shapes as shown on the SEM images in the figure 9.

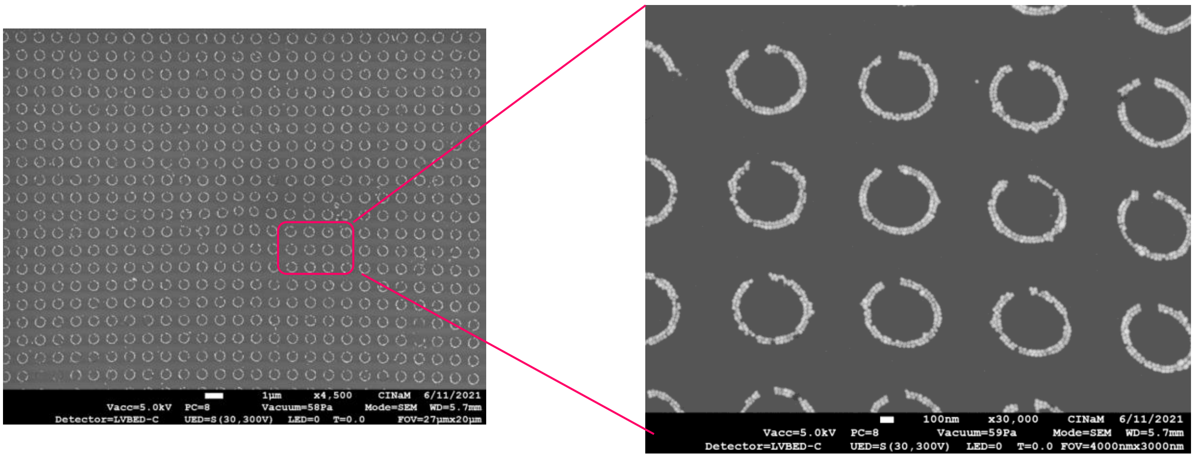

Figure 9: SEM images of the assembly of the silver nanocubes within the PDMS template carried out by capillary process.

The final step is the transformation of the silver nanocubes into a continuous material to form uninterrupted nanorings within the PDMS templates. For that, ongoing tests are performed with the PDMS molds. However, previous tests were carried out with nanocubes deposited on simple silicon substrates in order to optimize the process and have shown that just by a heating process at 220°C for 3 minutes, nanocubes that are closed to each other seems to be transformed into continuous material.

4. CONCLUSION

This research work shows the enhancement of absorption at optical frequencies by not only designing a metasurface made of silver split-rings with realistic geometric parameters reaching an absorption peak at a wavelength of 1500 nm, but also providing a first proof of concept of those tunable circular nanorings entirely made by scalable bottom-up approaches. Indeed, the parametric study performed by FDTD simulations in addition to the study of the pattern periodicity have led to a set of parameters showing enhancement of the absorption properties at a wavelength of 1500 nm. This motif has been then realized by a self-assembled technique of silver nanocubes into PDMS templates. Ongoing optical measurements and numerical simulations of an extensive array of nanorings are performed to confront experimental results to simulations.

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