Plasmonic nanoparticles self-organization in chiral liquid crystals

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Abstract

In this work we are proposing a bottom-up approach for the assembling of a functional metamaterial based on gold nanoparticles-doped chiral smectic liquid crystal. Nanoparticles (NPs) inclusion in such a system does not compromise the typical periodic texture characterizing this liquid crystalline phase. On the contrary, first experimental observations clearly suggest that NPs present a periodic organization in the liquid crystal template, providing striking reconfigurable features under the action of external stimuli. In addition, bringing gain in these self-organized structures can lead to low-loss architectures where the plasmonic responses can be tailored and controlled.

Introduction

The fabrication of metamaterials operating at optical frequencies is a very challenging topic, but with very promising prospectives. In the last years the “bottom-up” techniques based on the self assembling of organic building blocks, such as liquid crystals [1] and copolymers [2], started to be considered as an effective alternative to the lithography-based approaches. The advantages are many: the higher efficiency, the lower costs and the possibility to realize a large variety of two dimensional and three dimensional ordered structures with periodicity going from few nanometers to hundred microns.
In particular, the use of liquid crystal as a host template for nanoparticles embedding represents a further advantage because, besides their spontaneous order at the molecular scale, they are also reconfigurable by means of external fields (i.e. electromagnetic, thermal, mechanical fields).
The optical response of the resulting functional material depends on the type, on the shape and on the size of the nanoparticle resonator but also on the dielectric properties of the surrounding medium. It means that when the host template is a liquid crystal the optical properties of the system can be steered by external fields. In reference [3], [4] and [5] some different tunable systems obtained combining plasmonic metals and liquid crystal are discussed. The electromagnetic material properties of nanosphere dispersed liquid crystals may be calculated by employing the Maxwell Garnet mixing rule for a medium with three distinct regions: the host liquid crystal, the silica shell, and the noble metal core. It is the combination of the permittivities at the appropriate resonances, in conjunction with the field-induced permittivity change in the liquid crystal host that give rise to the effective refractive index of nanosphere dispersed liquid crystals.
In this work we are considering thermotropic liquid crystals whose order degree is temperature dependent. The smectic phase besides the orientational order of molecules presents a translational order, resulting in a layered structure with a nanometric interlayer spacing comparable with molecule length. The spontaneous formation of a nanostructured periodic matrix makes smectic liquid crystals suitable candidates to embed and organize nano-sized objects such as metallic nanoparticles. Moreover in the smectic phase molecular motion in the direction perpendicular to the layers results reduced respect to the motion within each layer, therefore smectic phase behavior results more solid-like. It has been shown that smectic liquid crystal visco-elastic properties are able to prevent nanoparticles aggregation thus promoting their dispersion inside the host medium to very high metal

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volume fraction [6]. An important fact is that effective electromagnetic scattering and resonance properties are only achieved when the density of resonance units or nanoparticles is high. Systems with nanoparticles concentrations below 10% in volume (and not weight) are usually not effective for parameter engineering. Here, we discuss the basic problem of material and sample fabrication: density of resonant units, uniformity over large areas and tunability of the effective electromagnetic response.

Materials and methods

The liquid crystal used in this work is a chiral smectic C (C* phase) in which the molecules are tilted to respect to normal to the layers. While the layers pile up the molecules turn forming a helical structure characterized by a spontaneous pitch Z.
A particular configuration for a smectic C* phase confined between two aligning surfaces has been considered. When the periodicity of the helical structure is smaller than the cell thickness a large-area texture characterized by a periodical array of lines is obtained (Fig 1a).

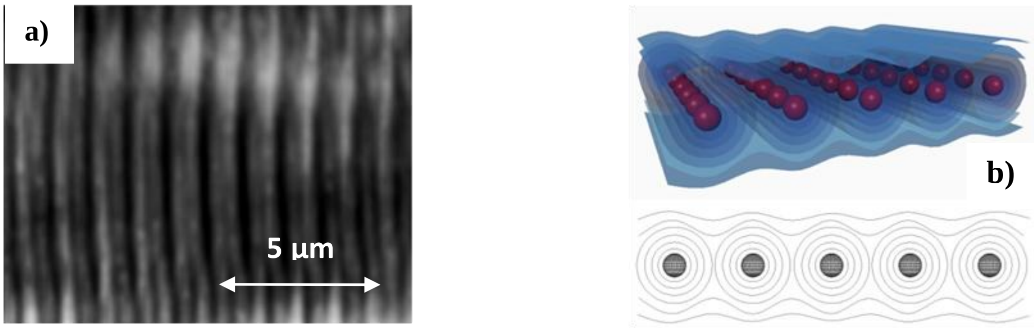

FIG 1: (a) Optical microscopy image of a typical periodic texture observed in smectic C* liquid crystal including gold nanospheres with a diamteter of about 12 nm. (b) Sketch of a possible organization of nanospheres in the chiral smectic liquid crystal template: Nanoparticles lay along periodic line defects, thus forming equidistant long chains.

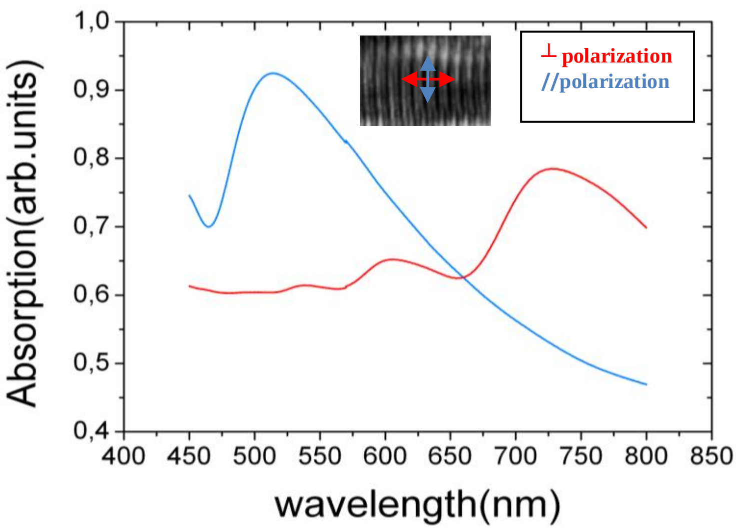

FIG 2: Absorption spectra for a smectic C* sample embedding gold nanospheres obtained by illuminating with linear polarized light parallel and perpendicular to the periodic structure.

It has been interpreted as defect lines and planes resulting from the connection between the helical structure in the bulk and the parallel alignment imposed by the strong anchoring at the top surfaces [7].

A similar texture has been already observed in a different system where a thin film of a non-chiral smectic is deposited in air on a crystalline surface [8]. In this case the appearance of defects lines is due to the conflicting anchoring condition imposed by the bottom and the open surface.
In Fig.1 is shown the sketch of a possible configuration of nanoparticles in the smectic C* template under study. The smectic layers deformation induced by boundering effects create defect lines in correspondence of which nanoparticles are located. In fact, it is well known that nanoparticles and more in general colloids interact with disclinations and defects present in liquid crystal phases [9] and under opportune energetic conditions they can be trapped within defects [10].
Absorption spectra related to this systems show a polarization dependence that is consistent with an anisotropic organization of nanoparticles. The same behavior has been indeed observed in structures like dimers, trimers and nanoparticles chains [11,12]. In Fig. 2 absorption spectra are obtained by illuminating with linear polarized light parallel and perpendicular to the periodic microstructure.

Conclusions

Complex assemblies of nanoparticles in liquid crystalline matrices can be achieved by self-organization mechanisms based on competition between liquid crystal viscoelasticity and van der Waals interaction between metal nanoparticles. In such a hybrid approach different structuring length scales are accessible. Most of the metamaterials designs are based on dense particles arrangements. Nanoparticles arranged in parallel long chains might lead already to interesting electromagnetic properties if geometrical parameters can be varied over a wide range.

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