Plasmonic properties of light sculptured structures including liquid crystals doped with metal nanoparticles

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Abstract

Polymeric templates favour the self-organisation of liquid crystal materials doped with metallic nanoparticles. A first spectroscopical characterization of the fabricated samples is reported. The plasmonic response obtained from the structures is polarization sensitive and can be somehow tuned by applying external fields. The research is oriented to the fabrication of devices with meta-material properties.

1. Introduction

In the last decade, the use of noble metal nanoparticles (NPs) for research purposes has drastically increased, the reason of this wide interest being related to their plasmonic properties [1]. Indeed, theoretical studies confirm that, under particular conditions, shape and spatial distribution of particles can acquire a strong influence on electromagnetic propagation [2] and, hence, new ways for realizing the so-called "metamaterials" have opened. These have been predicted in 1969 by Veselago [3] and represent materials which gain peculiar electromagnetic properties (e.g. negative refractive index) from their structure, rather than from their chemical composition. Thanks to recent advances in nanofabrication, first examples of such meta-materials, which exhibit particular functionalities at optical frequencies, have been realized [4]. However, the success of results obtained up to now is limited by the typical size of devices that can be fabricated, which is actually very small (few square millimetres). Alternative approaches are emerging, which propose the use of self-assembling materials in order to overcome this issue and obtain the sought for greater structures, with less difficulty [5]. An ambitious project is to combine metallic units with host materials whose dielectric properties can be tuned by an external control; indeed, a modification of the dielectric behavior of the host could correspond to a tuning action of the plasmon resonance frequency [6]. In this regard, liquid crystals (LC) represent good candidates as host materials. In this work, we report our attempts to realize structures where metallic NPs are dispersed in a dielectric material with tunable features.

2. Polymeric templates as multi-function host structures

POLICRYPS diffraction gratings are polymer–liquid crystal–polymer–slice periodic structures that exhibit high quality morphological features and functionalities [7]. They can be fabricated by means of a very flexible holographic procedure: structuring length scales can easily range from tens of microns to hundreds of nanometers [8]. One of the main advantages of POLICRYPS consists in its ability to induce an alignment of the contained liquid crystal (LC) compound. POLICRYPS utility has been demonstrated for several LC materials including: nematic, cholesteric and smectic liquid crystals [9]. As an example, in Fig. 1, micrographs of a POLICRYPS template infiltrated with Cholesteric Liquid Crystals (CLCs) are reported.

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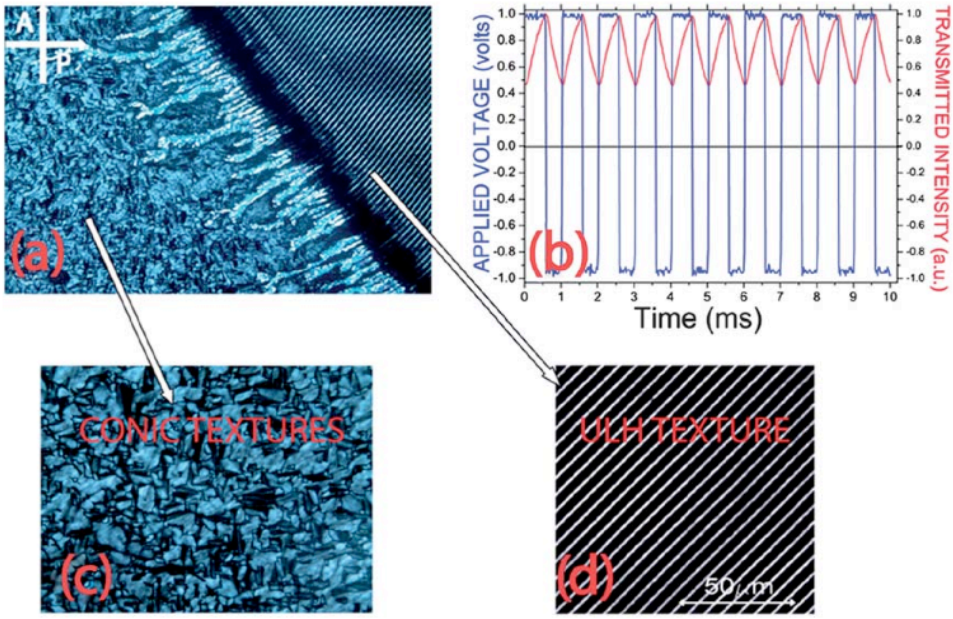

Fig. 1. Polarizing optical microscope view of a POLICRYPS template filled with short pitch CLC at the edge of the grating area (a). The high magnification of the random oriented CLC area is reported in (c) while the CLC area aligned in ULH geometry is shown in (d); its electro-optical response is reported in (b).

These are LCs possessing a helical super-structure; they organize in layers with no positional order of molecules within each layer, but characterized by a director axis, whose orientation smoothly changes from layer to layer, the reorientation of the director axis tending to be helicoidal, with a pitch that can vary in the range 0.1–20 mm. A particular CLC configuration is obtained when the cholesteric helices are uniformly aligned in the plane of the two confining substrates (Uniform Lying Helix (ULH) configuration). We point out the capability to align the CLC in a ULH texture, exhibited by the POLICRYPS template: Fig. 1a is a Polarizing Optical Microscope (POM) micrograph of the sample at the edge of the photo-sculptured grating area, which shows, on the left, the existence of a standard focal conic texture, induced by a random distribution of the helical axes (high magnification in Fig. 1c). On the right, the ULH geometry induced by the POLICRYPS structure is well evident (high magnification in Fig. 1d). An electro-optical characterization of the area depicted in Fig. 1d is shown in Fig. 1b. An external voltage (1 KHz square wave), applied across the cell perpendicularly to the helix axis, induces an in-plane tilt of the optical axis of the CLC, aligned in a ULH texture; the tilt is inverted if the polarity of the electric field is reversed. The magnitude of the transmitted intensity (red curve in Fig. 1b) is proportional to the applied voltage that induces the in-plane rotation of the sample optical axis, with a characteristic time that falls in the microsecond range.
Use of CLC materials can represent an indirect advantage for obtaining ordered assemblies of metallic NPs. Indeed, a literature search shows that NPs tend to organize themselves to avoid the ordering action of LCs; they generally flee in energetic convenient areas (e.g. along disclinations of LC textures) as demonstrated in [10] and [11]. By using a POLICRYPS template for aligning a CLC material, doped with metallic NPs, it is possible to obtain a multilayer device showing plasmonic resonances.

3. Plasmonic properties of fabricated samples

A Spectroscopical characterization of POLICRYPS templates infiltrated with NPs doped liquid crystals has been performed. Samples have been illuminated with linearly polarized white light impinging at normal incidence (wavelength varying in the range 350-1100nm). Transmitted spectra show absorption peaks in the same wavelength range where the plasmonic resonances of the involved NPs are expected. The application of external stimuli (temperature and electric fields) has somehow evidenced a

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dependence of this response: shape and position of the peaks depend on the amplitude of the applied electric field and/or on the actual value of the sample temperature. It is interesting to underline that the observed behaviour is polarization dependent. This derives from the fact that our polymeric templates are basically diffraction gratings. Indeed, a standard POLICRYPS (without NPs) strongly diffracts p-polarized light while the diffraction efficiency is negligible for the s-polarized light. In presence of NPs, the structure behaves in a similar way with the p-polarized light while exhibiting a plasmonic response of the metallic NPs with s-polarized light.

4. Conclusion

Results reported in this paper show that, by infiltrating POLICRYPS templates with liquid crystals doped with metallic NPs, it is possible to obtain multilayer plasmonic systems that exhibit a polarization sensitive plasmonic response. Moreover, performed experiments have evidenced that this response is dependent on the application of an external (electric or temperature) field. Results can be considered as a first step in the direction of obtaining tunable devices with metamaterial properties. Further investigations will be devoted to evidence how the variation of critical structure parameters (periodicity of the grating or NPs concentration) can influence the functionalities of the device.

References

[1] U. Kreibig, M. Vollmer, “Optical Properties of Metal Clusters”, Springer-Verlag, Berlin, Germany (1995).

[2] C. Rockstuhl, F. Lederer, C. Etrich, T. Pertsch, T. Scharf, Phys. Rev. Lett. Vol. 99, 017401 (2007).

[3] V.G. Veselago, "The electrodynamics of substances with simultaneously negative values of e and m,". Sov. Phys. Usp, vol. 10, 4, 509 (1968).

[4] J. Valentine, S. Zhang, T. Zentgraf, E. Ulin-Avila, D.A. Genov, G. Bartal and X. Zhang, "Three Dimensional Optical Metamaterial Exhibiting Negative Refractive Index", Nature, vol. 455, 376 (2008).

[5] EU Project: “Self-organised nanomaterials for tailored optical and electrical properties (Nanogold)”, FP7-NMP-SMALL-2008-228455, http://nanogold.epfl.ch, (2009-2012); EU Project: “Nanochemistry and self-assembly routes to metamaterials for visible light (Metachem)”, FP7-NMP-SMALL-2009-228762, www.metachem-fp7.eu, (2009-2013).

[6] P.A. Kossyrev, A. Yin, S.G. Cloutier, D.A. Cardimona, D. Huang, P.M. Alsing and J.M. Xu, “Electric Field Tuning of Plasmonic Response of Nanodot Array in Liquid Crystal Matrix”, Nano. Lett. 5, 10, 1978 (2005).

[7] R. Caputo, A. Veltri, C.P. Umeton, A.V. Sukhov, “Characterization of the diffraction efficiency of new holographic gratings with a nematic film–polymer-slice sequence structure”, J. Opt. Soc. Am. B, 21, 1939 (2004).

[8] L. De Sio, R. Caputo, A. de Luca, A. Veltri, A.V. Sukhov, C. Umeton, “In-situ Optical Control and Stabilization of the Curing Process of POLICRYPS Gratings”, App. Opt. 45, 3721 (2006).

[9] L. De Sio, S. Ferjani, G. Strangi, C. Umeton and R Bartolino “Universal Soft Matter Template For Photonic Applications”, Soft Matter (DOI:10.1039/C1SM05045A).

[10] M. Mitov, C. Portet, C. Bourgerette, E. Snoeck, M. Verelst, “Long-range structuring of nanoparticles by mimicry of a cholesteric liquid crystal”, Nature Mater. 1, 229 (2002).

[11] R. Pratibha, W. Park and I.I. Smalyukh, “Colloidal gold nanosphere dispersions in smectic liquid crystals and thin nanoparticle-decorated smectic films”, J. App. Phys. 107, 063511 (2010).

