

Soft matter template containing metallic subunits dissolved in self-organized materials

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Abstract

We report on the fabrication and characterization of a micro periodic structure realized in soft-composite materials containing gold nanoparticles. These are dissolved in cholesteric liquid crystals and then infiltrated in a passive polymer template, realized by combining an holographic step and a microfluidic etching process. The spectral behaviour of obtained structures has been studied in the UV-Vis range by varying the impinging probe light polarization. Correlation between the optical response and external perturbations (electric field, temperature) has also been investigated. These attempts are oriented to the fabrication of devices with tuneable metamaterial properties.

1. Introduction

Metallic particles show plasmonic resonances when excited with suitable electromagnetic radiation. The spectral position of these resonances can be modified by properly varying the size and shape of the utilized particles. This feature is very attractive for eventual applications and several cases have been already explored [1]. Despite obtained results are quite promising, only static devices have been fabricated up to now. 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 behaviour of the host material could yield a tuning action of the plasmonic resonance frequency. To this end, Liquid Crystals (LCs) are an outstanding example as an active dielectric medium: they combine self-organizing properties with fluidity, and can fulfill conditions imposed from outside, being quite responsive to a wide variety of external stimuli. LCs are made by anisotropic molecules possessing a long range orientational order, a very broadband (0.4 μm –12 μm , in light wavelength) range of birefringence and transparency, and a high susceptibility to AC, DC and optical fields [2]. Thanks to these properties, LCs can be used for realizing a wavelength-selective absorption shift of the plasmonic resonance, induced by an externally applied electric field. At the same time, LCs can be exploited as “host-fluid” for dissolving colloidal noble nanoparticles; however, one of their main drawbacks is represented by the fact that, in general, they require chemical and/or mechanical treatments to be aligned. Recently, we have reported on the realization of a periodic soft-composite template with a wide range of photonic applications [3] that can represent a solution to such drawback. By applying a microfluidic etching to a composite micro/nano grating, made of polymer slices alternated to films of well oriented LC (POLICRYPS), we can obtain a novel platform that is able to align and microconfine a large variety of liquid crystalline materials, without the need of any chemical and/or mechanical treatment. In this paper, we show that this platform can be used as well for efficiently aligning Cholesteric Liquid Crystals (CLC) doped with a small amount of gold nanoparticles.

2. Polymeric template

The wet etching process performed on a POLICRYPS structure is carried out by dipping the sample (without opening the cell) in a water solution of tetrahydrofuran (THF); the solvent enters the sample by capillary flow and acts as a selective agent, removing the LC and the unpolymerized component without affecting the regularity of the polymer slices.

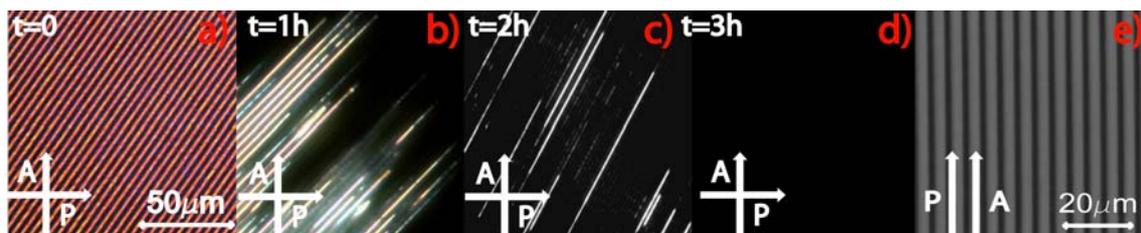


Fig 1: POM view of a POLICRYPS structure during the micro-fluidic etching process at different time scales (a-d). Polymer template after removing the NLC (e).

In Fig. 1, different optical microscope pictures (taken between crossed polarizers) show the sample during the emptying process: The micrograph in Fig.1a was acquired before immersing the sample in the solvent; Fig 1b,c,d shows a sample removed from the solvent respectively after 1, 2 and 3 hours. The completely black area in Fig. 1d confirms that the LC component has been completely washed out on removal of the sample from the solvent. In Fig. 1e is reported the polymer template after removing the NLC made of sharp polymer slices separated by empty channels

3. Experimental Results

In order to obtain a homogeneous mixture including metallic nanoparticles (NPs) and CLC, we have chosen the Harima gold nanopaste NPG-J (from Harima Chemicals, Inc.), generally used for other aims (e.g. ink-jet printing and laser sintering), and the BL095 CLC by Merck (helix pitch ~ 400 nm). The Au NPs have been mixed with CLC (about 20%wt) and then infiltrated, by capillarity, in the previously described polymeric template. The sample was kept at a fixed high temperature (~ 90 °C) during the whole filling process, thus keeping the CLC in the isotropic phase. By slowly (0.5 deg/min) cooling down the sample to room temperature, a self-organization process occurs, which orients the main axes of CLC helices parallel to the polymeric slices (Uniform Lying Helix (ULH) configuration) as shown in Fig 2.

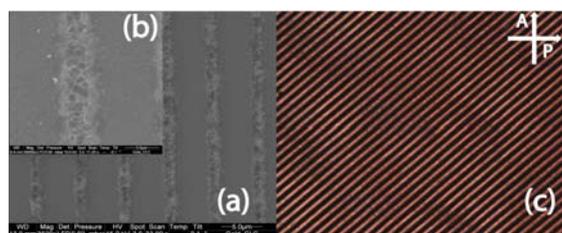


Fig 2: Scanning Electron Microscope (SEM) view (a) and high magnification (b) of the polymeric template filled with CLC and Au NPs. (c) is a Polarized Optical Microscope (POM) view of the structure

Despite the quite high concentration of Au NPs, the CLC exhibit a uniform alignment, with the helices very well organized between the polymeric slices. The CLC exhibits good “host-fluidity” properties for the Au NPs; at the same time, thanks to the high degree of the order, the CLC phase is weakly perturbed by the presence of the AU NPs. As shown in the SEM view of Figs. 1a,b, there is no evidence of Au clusters, while the helices appear like “wrapped” by the quasi-monodispersed Au particles. The optical response of the structure has been investigated by probing the sample with a linearly polarized white light (wavelength in the range 350-1000nm, at normal incidence). Obtained results are reported in Fig 3. Due to the presence of a grating structure, p-polarized light experiences a strong refractive index contrast ($n_e > n_p$) and is, consequently, strongly diffracted. In this case, light transmission is almost suppressed (diffraction pattern of Fig. 3a, magenta curve). On the other hand, s-polarized light is highly transmitted in the whole analysed range, because the experienced refractive index modulation is quite limited ($n_o \approx n_p$) and the grating is almost absent (diffraction pattern of Fig. 3a, blue curve; in the above sentences, n_p , n_e and n_o refer respectively to the polymer refractive index, to the extraordinary and ordinary refractive indices of the CLC material).

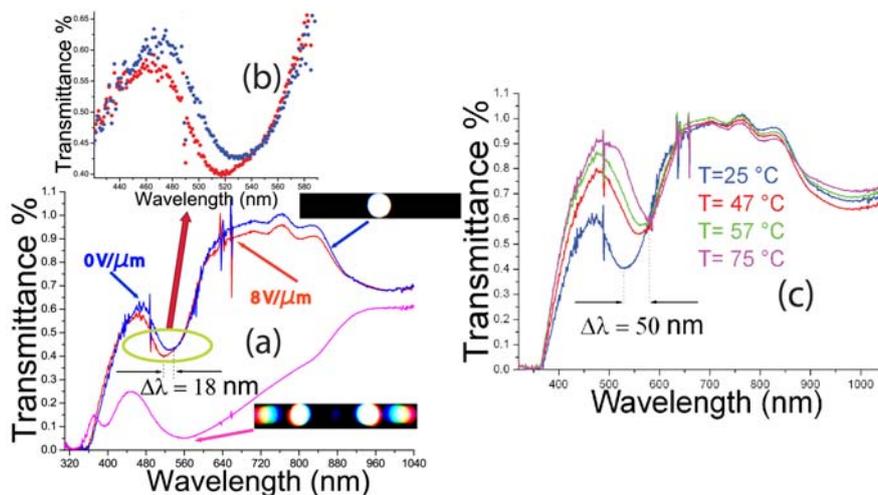


Fig. 3: Spectral response of the sample versus the external electric field (a) and its higher magnification (b) while the temperature dependence is reported in (c)

In the blue curve (Fig. 3a), a pronounced plasmonic absorption peak (at $\lambda=530$ nm and with an extinction coefficient of 0.2) due to the presence of isolated Au NPs can be observed. The particular position of the absorption peak is determined by the collective dielectric response of the entire medium (Au NPs/CLC), where plasmons and electronic dipole coupling are involved. The application of an external electric field (frequency 1 Khz, square wave), across the cell, and perpendicularly to the helix axes, induces an in-plane tilt of the optical axis of the CLC (aligned in a ULH texture), with a consequent variation of the CLC refractive index. A modification of the dielectric behaviour of the host material corresponds to a tuning action of the plasmonic resonance frequency, as observed in Fig. 3a (red curve): the absorption peak is blue shifted from $\lambda=530$ nm to $\lambda=512$ nm. This is probably due to a decrease of the refractive index of the host material ($n_{\text{eff}} \rightarrow n_o$). On the contrary, by increasing the temperature of the sample, the CLC helices tend to unwind with a consequent variation of the CLC pitch. This variation induces a red shift (Fig. 3c) of the plasmonic resonance of about 50 nm probably due to a change of the inter-particle distance.

4. Conclusion

We have reported on the realization and characterization of a soft-matter periodic template containing a composite mixture of CLC and Au NPs. The CLC material acts as a “host fluid” for the Au NPs and, at the same time, thanks to its birefringence, enables to vary the refractive index of the surrounding medium. This variation has a strong influence on the position of the plasmonic absorption peak of NPs.

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