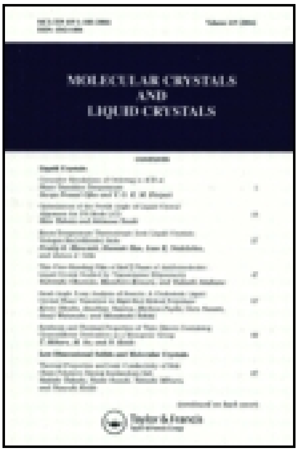

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Plasmon Resonance Tunability of Gold Nanoparticles Embedded in a Confined Cholesteric Liquid Crystal Host

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Plasmon Resonance Tunability of Gold Nanoparticles Embedded in a Confined Cholesteric Liquid Crystal Host

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Gold nanoparticles have been dissolved in a cholesteric liquid crystal and then infiltrated in a micro-periodic polymeric structure. This has been realized by combining a holographic step and a microfluidic etching process. The spectral behavior of the nano-composite soft-structure has been investigated in the UV-Vis range for two different polarization directions of an impinging probe light and in presence of external perturbations (electric field, temperature variation). Obtained results show a highly tunable plasmonic response of the material.

Keywords Cholesteric liquid crystals; diffraction gratings; metallic nanoparticles; plasmonic resonances

Introduction

Different approaches are actually exploited for realizing nanomaterials with peculiar features but, very often, pros and cons of each of them seem to be almost balanced, and the right choice can be hardly taken. When using a "top-down" approach, matter is the object of external actions that modify its structural properties; interference holography [1] and e-beam lithography [2] are examples of such an approach. In the first case, large structures can be realized, but their resolution is limited by the wavelength of the curing radiation. On the contrary, the electron beam can produce very resolute details, but the procedure is particularly cumbersome and time consuming so that the useful area of the obtained structure turns out to be very limited. When dealing with a "bottom-up" approach, functional nanostructures are organized by using a molecule-by-molecule arrangement: atoms and/or molecules self-assemble into a particular structure due to their peculiar properties. In the last years, metallic nanoparticles (NPs) have been used as building blocks for realizing a new generation of nanomaterials with peculiar, unusual, optical properties. In particular, gold and silver NPs show plasmonic resonances when excited by a suitable electromagnetic radiation in the visible portion of the spectrum. The spectral position of this kind of resonance can be modified by properly varying the size and shape of the utilized particles; this feature is attractive for possible applications and several cases have been already explored

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[3]. However, despite the obtained results being quite promising [4–7], only samples with static properties have been realized up to now. An ambitious project is to combine metallic units with host materials whose dielectric properties can be tuned by means of an external control; in this way, a modification of the dielectric response of the host material may yield a tuning action of the plasmon resonance frequency [8]. An outstanding example of such an active dielectric medium is given by Liquid Crystals (LCs): they combine self-organizing properties with fluidity, and can fulfill conditions imposed from outside, being quite responsive to a wide variety of external stimuli. Moreover, they have been already exploited as a "host-fluid" for dissolving colloidal noble nanoparticles [9]. Unfortunately, a drawback exists due to the circumstance that, in general, LCs require chemical and/or mechanical treatments to be aligned. In addition, the order degree of the LC director is lowered by the inclusion of nanoparticles; therefore, their concentration in the host LC must be limited to few percents [10,11]. Recently, we have reported on the realization of a periodic soft composite structure, with a wide range of photonic applications, which might represent a solution for the above drawbacks [12,13]. By a microfluidic etching of a composite micro-grating, made of polymer slices alternated to films of well oriented LC (POLICRYPS) [14,15], we can realize a polymeric platform that is able to align and micro-confine a large variety of LC materials, without the need of any chemical and/or mechanical treatment. In this paper, we show that the same platform can be utilized for efficiently aligning Cholesteric Liquid Crystals (CLC) doped with gold nanoparticles, as well.

Sample Preparation

In order to obtain a homogeneous mixture of metallic nanoparticles (NPs) and CLC, we have used the Harima gold nanopaste NPG-J (from Harima Chemicals, Inc.) and the BL095 CLC by Merck (helix pitch $\approx$ 400 nm). NPG-J contains 55 wt% of Au NPs, with an average diameter of about 10 nm and a plasmonic absorption peak in solvent (naphthen) at $\lambda =$ 525 nm. The capping agent used to avoid clustering between Au NPs is not known du to the fact that the NPG-J nanopaste is a product patented by Harima Chemicals, Inc. However, notwithstanding the large content of Au NPs, the material is liquid at room temperature and, if diluted with Chloroform, it shows a dark red coloration that is a strong indication of the mono-dispersion of Au NPs. In our experiments, this material has been mixed with the CLC in high concentration (about 20 wt%) and then infiltrated, by capillarity, in an empty polymeric template of $L\approx 10\mu$m thickness and $\Lambda\approx 6\mu$m pitch. The sample was kept at fixed high temperature ($\sim$90°C) during the filling process, thus keeping the CLC in the isotropic phase; then, by slowly (0.5 deg min^{-1}) cooling down the sample to room temperature, a self-organization process occurred, which induced the axes of CLC helices to be oriented almost parallel to the polymeric slices, in a uniform lying helix (ULH) configuration [12]. Figure 1(a) shows a polarized optical microscope (POM) micrograph of the sample at the edge of the photo-sculptured grating area; on the left, the photo puts into evidence the existence of a standard focal conic texture, induced by a random distribution of the helical axes. On the right, the polymeric structure induces a ULH geometry (Fig. 1(b)), as demonstrated by the presence of a selective reflection (stop band), typical of a short pitch CLC (Fig. 1(c)). Despite the quite high concentration of Au NPs, the high magnification in Fig. 1(b) indicates that the CLC is uniformly aligned, with very well organized helices confined between polymeric slices. This is a clear indication that the CLC exhibits good "host-fluidity" properties for the Au NPs; at the same time, its high degree of order indicates

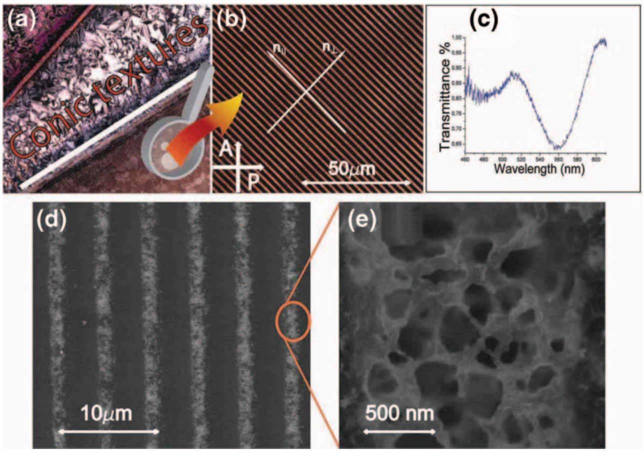

Figure 1. POM view of the polymeric template filled with CLC and Au NP mixture at the edge of the grating area (a). The high magnification of the CLC and Au NPs area aligned in a ULH geometry is shown in (b) while its typical reflection notch is reported in (c). EBSD view (d) and high magnification (e) of the polymeric template filled with CLC and Au NPs.

that the CLC phase is weakly perturbed by the presence of Au NPs. The obtained structure represents, in our opinion, the successful combination of a "top-down" approach (polymeric template fabrication) with a "bottom-up" one, represented by the self-organization of Au NPs in CLC helices.

To investigate the effects produced by the presence of Au NPs embedded in the microstructure, we first tried to figure out their distribution inside the CLC host by performing a scanning electron microscope (SEM) and an electron back-scattering diffraction (EBSD) characterization of the sample. In particular, the EBSD analysis is valuable to distinguish gold from other materials, since the yield of backscattered electrons increases with the specimen atomic number (Z); in our case, the presence of gold ($Z = 79$) produces a high contrast with the polymer microstructure (a thiol based system with $Z \approx 18$). As shown in the EBSD view of Fig. 1(d), the bright stripes confirm the presence of Au along the microchannels only, while in the high magnification picture (Fig. 1(e)), we can notice that CLC branches are literally "wrapped" by densely packed Au particles. Considering the size of the involved NPs (~10 nm), the SEM resolution is not able to show their morphological details.

Experimental Characterization

In order to study the influence of Au NPs on the optical properties of the whole structure, we have investigated its spectral response by probing the sample with linearly polarized white light (wavelengths in the range 350–1000 nm) at normal incidence; obtained results are reported in Fig. 2. It is evident that p-polarized light is strongly diffracted and its transmission is almost suppressed (diffraction pattern in the lower part of Fig. 2(a) and magenta curve respectively).

On the other hand, s-polarized light is highly transmitted in almost the whole range (diffraction pattern in the upper part of Fig. 2(a) and green curve respectively). This behaviour has already been observed in the past with a similar structure [16] and can be

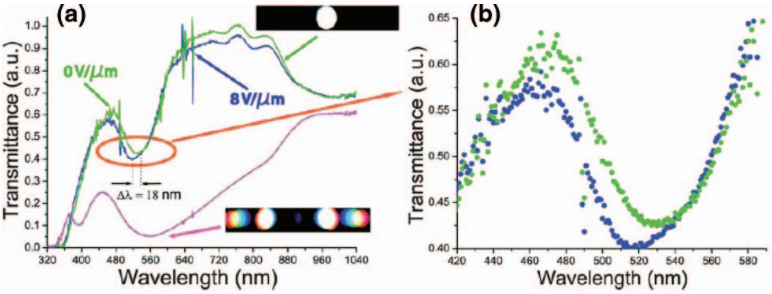

Figure 2. Spectral response of the sample for two values of the external electric field (a) and its higher magnification detail (b).

easily explained by supposing that CLC helices lay, in average, along the channels of the polymeric template. It is reasonable to assume, therefore, that two different effective refractive indices exist: n_L (whose value can be estimated to be $\sim$1.64), quite different from the polymeric refractive index n_p ($\sim$1.54), which is experienced by light whose electric field is perpendicular to the channels (p-wave), and n_s whose value can be estimated to be $\sim 1.56 \approx n_p$, for light whose electric field is parallel to the channels (s-wave). The above rough estimation of n_s and n_L has been made by averaging differently weighted ordinary and extraordinary refractive indices (n_o and n_e) of the CLC for two different polarizations. Due to the alternation of n_L and n_p indices, the grating structure is therefore experienced by the p-wave only. Incidentally, the quite big difference between n_L and n_s values is confirmed by the noticeable birefringence shown by the sample (Fig. 1(b), picture taken between crossed polarizers). In the green curve of Fig. 2(a), a pronounced absorption peak at $\lambda = 532$ nm, with an extinction coefficient of 0.2 can be observed. This peak cannot be attributed to any diffractive mechanism, since the structure appears optically homogeneous ($n_s \approx n_p$) to the incoming s-wave. Both the spectral position and the narrow width of the measured peak suggest, instead, that it is due to the Au NPs dispersed in the CLC host and, more precisely, to their localized plasmon resonance. This hypothesis is supported by similar results reported in the literature [17] and observed in different systems where Au NPs are also involved [18]. Even if physically remarkable, this result is not outstanding in itself. It is quite interesting, on the contrary, the circumstance that the plasmonic response of the investigated composite nanomaterial is also tunable. This has been demonstrated by applying an external electric field (8 V μm^{-1}, frequency 1 kHz, square wave) across the cell, perpendicularly to the helix axes. This field induces an in-plane tilt of the optical axis of the CLC (aligned in a ULH texture), with a consequent variation of the n_S refractive index of the CLC, experienced by s-wave. This index variation is directly related to the tuning of the plasmon resonance frequency. Indeed, the optical properties of spherical particle dispersions can be predicted by the Mie theory [8] through the expression of the extinction cross section:

$$\sigma_{ext}(\omega) = 9\frac{\omega}{c}\varepsilon_m^{3/2}V_0\frac{\varepsilon_2(\omega)}{[\varepsilon_1(\omega)+2\varepsilon_m]^2+\varepsilon_2(\omega)^2} \tag{1}$$

where $V_0 = (4\pi/3)R^3$ is the nanoparticle volume, R being its radius, ω is the angular frequency of the impinging radiation, ε_m is the dielectric function of the medium surrounding the metallic nanoparticles, and ε_1, ε_2 are the real and imaginary parts of the dielectric function of the metallic nanoparticles respectively. Based on expression (1), the spectral position of the plasmonic absorption peak of small and isolated metal particles depends on the refractive index of the surrounding medium, according to the resonance condition (that minimizes the denominator):

$$\varepsilon_1(\omega) = -2\,\varepsilon_m \tag{2}$$

A modification of the dielectric function of the host material corresponds, therefore, to a tuning action of the Plasmon resonance frequency. In our case, when applying the external electric field, the impinging probe light experiences a decreasing value of the refractive index of the CLC (from n_s to about n_o; typically from 1.56 to 1.5). Following equation (2), the resonance condition is fulfilled for higher (negative) values of $\varepsilon_1(\omega)$. It is well known that, in the visible range, the real part of the electric permittivity of Gold nanoparticles increases with frequency [19]; therefore, fulfillment of equation (2) takes place for higher values of ω a condition that yields a blue shift of the plasmonic absorption peak. This hypothesis is confirmed by results shown in Fig. 2(b) (higher magnification of the highlighted region of Fig. 2(a)): at room temperature, the absorption peak is blue shifted from $\lambda = 532$ nm (blue curve Fig. 2(b)) to $\lambda = 514$ nm (red curve Fig. 2(b)), with a consequent tunability range $\Delta\lambda = 18$ nm.

An additional verification of the tunability of the plasmonic response of our composite structure has been obtained by varying the temperature of the sample; results are reported in Fig. 3. By means of a miniature oven (CaLCTec S.r.l.), it was possible to vary the sample temperature from 25°C up to 75°C; to this change of temperature, a red-shift of the plasmonic absorption peak corresponds in the range from 528 nm to 581 nm (Fig. 3, inset). It is well known [20] that the pitch p of chiral liquid crystals elongates with temperature; if we assume that the CLC helices are wrapped by Au NPs, the consequence of this elongation is an increase of the inter-distance between neighboring metal NPs. It has been demonstrated that the plasmon response of NP arrays depends on particle size and density [4,21]; results show that, for densely packed metal NPs, the absorption peak is quite broad and is centered in the blue–green range, while this peak slightly reduces its width and shifts to the red in the case of well separated NPs. Indeed, as observed by Kinnan and Chumanov [22], when NP aggregates are considered whose size is comparable to the wavelength of the incoming

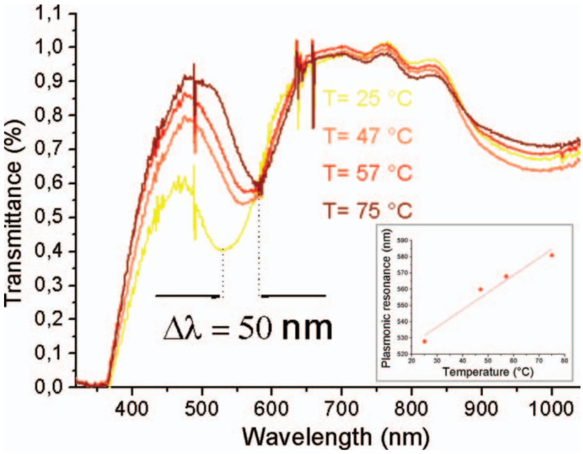

Figure 3. Spectral response of the sample versus its temperature. In the inset, the plasmonic peak position has been plotted as a function of the sample temperature.

radiation, different areas of the aggregates experience different phases of the incident radiation; thus, higher multipolar modes (quadrupolar, octupolar and even hexadecapolar) have to be taken into account. Given that the excitation frequency of these higher modes is larger than the excitation of the dipolar one, a macroscopic broadening of the plasmon peak occurs which has its center in the blue region of the electromagnetic spectrum. On the contrary, single, small-sized, NPs, when hit by the incoming radiation, experience the same phase of the electromagnetic wave on their whole area. In this condition, NPs behave as simple dipoles: the plasmonic peak width is quite narrow and, depending on the particle size, it is centered in the green–red part of the electromagnetic spectrum. Based on the above considerations, the temperature dependent shift of the plasmonic resonance observed in our sample can be explained in terms of a temperature induced passage from densely packed to mono-dispersed Au NPs.

Finally, another characterization has been performed by applying both an electric field and temperature variations to the sample. Indeed, due to the high difference existing between n_p and n_L, when probed with p-polarized light, the structure behaves as a diffraction grating. As such, by applying an external electric field, we expect a modification of its diffractive properties. In particular, if the induced director reorientation along the electric field direction lowers, the refractive index modulation and the intensity of diffracted beams decrease. Moreover, as suggested by above results, a temperature increase reduces the size of Au NPs aggregates; this corresponds to a higher "fluidity" of the (CLC + Au NPs) system and, then, to a reduction of the grating response time when the external electric field is applied. In order to verify this hypothesis, we kept the sample at different temperature values and, for each value, we monitored the temporal behavior of the first diffracted beam intensity under the application, across the cell, of an electric field. Results of these experiments are depicted in Fig. 4, where several curves illustrate how the system behaves at different temperatures. The abrupt changes in the diffraction efficiency values show the field-on and field-off conditions for the various reported curves. In the inset of Fig. 4, the switching time values are plotted versus sample temperature. At room temperature, the grating shows a very slow response ($T = 25°C$, $\tau_{sw} \approx 200$ sec.). The situation strongly improves when the sample is kept at high temperature ($T = 65°C$, $\tau_{sw} \approx 4$ sec.). As suggested above,

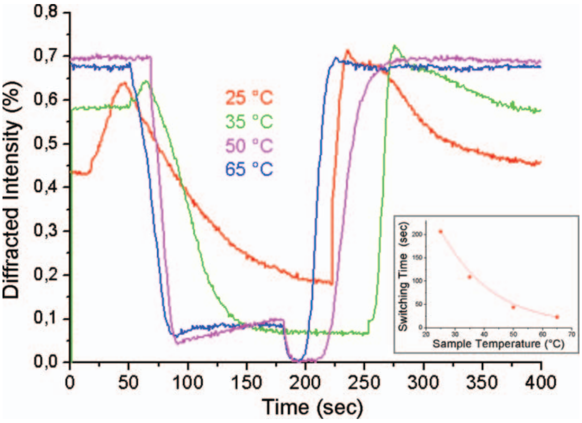

Figure 4. Temporal behavior of the sample at different temperature values and under the application of an external electric field. In the inset, the switching times have been plotted as a function of the sample temperature.

in this case we expect a better mobility of the Cholesteric molecules and hence shorter reorientation times due to the smaller size of the Au NPs aggregates.

At the moment, the reason why a change in shape and size of these aggregates takes place is not completely clear but further experiments are already on course for unveiling the real interaction between the CLC phase and Au NPs.

Conclusions

In conclusion, we have reported on the realization and characterization of a soft-matter periodic structure containing a composite mixture of CLC and Au NPs. For them, the CLC material acts as a "host fluid" whose refractive index can be varied in a broad range, by utilizing both external electric fields and temperature variations. This has a strong influence on the position of the NPs plasmonic absorption peak, which exhibits, consequently, a broad tunability. Results, enable to exploit the concept of "active plasmonics". On the other hand, when the system is utilized as a diffraction grating, it is possible to measure its switching time; measured values strongly depend on temperature. They are, indeed, quite long at room temperature but strongly reduce at higher temperatures. This is most probably due to the change of size of Au NPs aggregates that takes place at high temperature. As a proof of concept, this is the first step towards the realization of a new generation of nanostructured materials with tunable optical properties.

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