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Effects of Gold Nanoparticle Dispersion in a Chiral Liquid Crystal Matrix

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In this article, we report experimental studies on the effect of gold nanoparticle dispersion in a cholesteric liquid crystal matrix. Besides deeply affecting liquid crystal structural order upon inducing phase transition toward unexpected smectic-like phases, the presence of nanoparticles causes important changes in the liquid crystal electric properties, increasing liquid crystal conductivity and influencing ions diffusion.

Keywords Gold nanoparticles; phase transitions; smectic phases

Introduction

Phenomena associated to the nanoparticle dispersion in liquid-crystalline matrices are of growing interest in the soft condensed matter scientific community. Because of their unique properties, liquid crystals (LCs) are indeed considered suitable candidates for the realization of bottom-up systems including plasmonic nanoparticles (Au, Ag, and Pt).

The idea is to exploit their intrinsic order and the nanoparticle-host interactions to guide nanoparticle spatial organization [1–5]. Moreover liquid crystal reconfigurability would allow the realization of structures characterized by tunable plasmonic properties [6,7]. Many efforts have been done toward the fulfillment of these goals but still some problems remain; one of the most remarkable is related to macroscopic plasmonic properties that can arise only for high concentration of nanoparticles (10% filling volume fraction) because of the importance of relevant collective effects. On the other hand, nanoparticle dispersion can deeply modify liquid-crystal host properties. The improved performances of nanoparticle-doped LCs find their application into display technology [8], in this case, even a small amount of nanoparticles can be sufficient to obtain satisfactory results.

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It has to be also considered that, depending on nanoparticles size, nature, and surface treatment, above a certain concentration they can introduce distortion in the liquid crystal alignment [9,10]. In this article, we will show that a small concentration of gold nanoparticles can induce a deep structural change in a chiral nematic liquid crystal.

The observation of fun-like textures typical of smectic phases have been observed [11] in different confining geometries. Moreover an X-ray analysis confirms the presence of a smectic order within the nanoparticle-doped samples [12].

Current measurements are also reported. They show that the presence of nanoparticles and their aggregates have an important role in the charge transport mechanisms present in the doped liquid crystal samples [13,14].

Experiments

The liquid crystal used in this work is the BL094 (by Merk). It is characterized by the following phase sequence: S-Ch$<-20^{\circ}$C—*Ch–I* 73.5°C where S, Ch, and I indicate solid crystalline, cholesteric, and isotropic phase respectively. Gold nanoparticles (Au NPs, diameter 12 nm) have been synthesized in water [15] and then transferred to ethanol. Their external surface is surrounded by an electrostatic capping made by citrate ions that prevent their aggregation in solution. The dispersion has been prepared by mixing the liquid crystal with the ethanol solution. The blend has been continuously stirred at a temperature of 50°C till the complete solvent evaporation. The final percentage of Au NPs was 0.5% wt.

The samples used in all the electric characterizations have been prepared by filling glass planar cells (provided by E.H.C. CO., LTD. TOKYO-JAPAN) with a thickness of 8 μm, whose inner side is covered with an ITO conductive layer (thickness 30 nm, resistivity 100 Ω/Υ).The cells have been filled while the liquid crystal host was in the isotropic phase, then the system has been cooled down to room temperature at a controlled rate (0.2°C/min).

For the electro-optical measurements, the applied field to the cell is a triangular signal with an amplitude of 20 V and a frequency of 1 Hz. The measurements have been performed by using a linearly polarized He–Ne laser.

For the current measurements, a simple series circuit composed by the cell sample and a load resistance ($R = 1.8$ MΩ) has been realized. The input signal was applied to the circuit, while the output signal was acquired at the load's edges. For signal generation, we used a waveform generator (Wavetek 195) connected to a high-voltage amplifier by Matsumoto, while for signal acquisition, we used an Agilent Infiniium oscilloscope (model 54832D MSD). X-ray diffraction data have been collected on a D8 advance Bruker Diffractometer/Reflectometer CuKa radiation (40 KV, 40 mA) equipped with a Dynamic Scintillation Detector Nal and with a Gobel mirror. The measurements have been made in reflection θ-2θ geometry at room temperature and the patterns have been recorded in the 2θ range from 1° to 10°, in steps of 0.004° and different counting time per step. The measurements have been performed on a drop deposited on a glass substrate and thermally dealt as described before for the cell-confined samples.

Induction of a New Phase

The most remarkable and evident change occurred in the Au–NPs-doped samples was the perturbation of the original liquid crystal organization. By observing the BL094 bulk phase, it is possible to see that normally the material shows a cholesteric phase at room temperature with a characteristic stop-band centered around 550 nm. By filling a planar cell, it is possible to obtain an aligned cholesteric phase whose helix axis is oriented

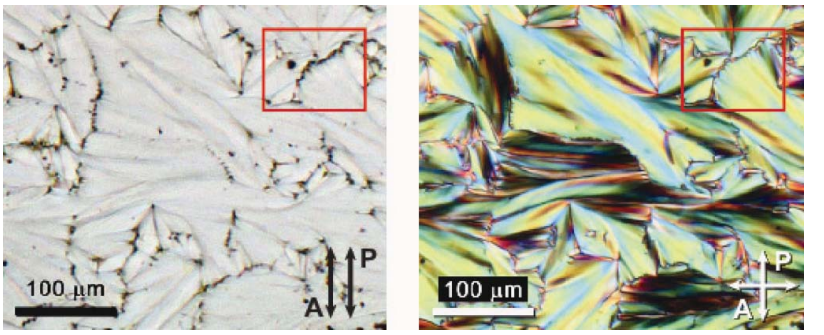

Figure 1. Pictures related to a sample of Au–NPs-doped BL094 confined in a planar cell acquired between parallel (a) and crossed (b) polarizers.

perpendicularly to the glass slabs. Liquid crystal alignment can be improved by bringing the sample above the LC-isotropic transition (73.5°C) and by cooling it down at a slow rate (0.2°C/min). In the case of the doped liquid crystal, the situation is much more complicated. The LC is still able to keep its original phase when the cell is filled at room temperature, while the thermal treatment described above is sufficient to completely disrupt the cholesteric order. It is evident since a first look to the samples: the selective reflection property of the cholesteric phase is lost, then they result totally opaque.

Figure 1 shows optical microscope pictures acquired for the doped sample after the thermal cycle. The fun-like textures exhibited are an important evidence of a deep structural change in the liquid crystal, they are indeed typical defects of most of the smectic phases. This represents a surprising results if we consider that the bulk phase sequence of the pure material does not comprehend any smectic phase. Textures of the same kind have been observed in several confining geometries: in planar cells (as already discussed), in free standing films created in the holes (1 mm × 1 mm) of a metallic grid (Fig. 2(a)) and in droplets deposited on different substrates (Fig. 2(b)).

These observations support the idea that irrespective of boundary conditions, guest nanoparticles play a key role in the structural organization of induced phases.

The hypothesis arisen by considering optical microscopy observation is supported by x-ray diffraction data (Fig. 3).

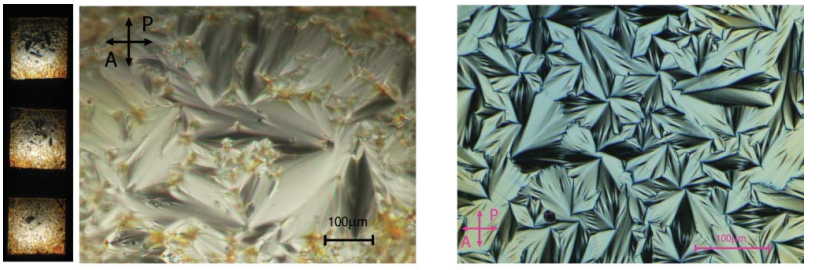

Figure 2. Optical microscope pictures of the smectic-like textures appearing in a droplet deposited in a freely suspended film (a) and on a glass substrate (b) of Au–NPs-doped BL094. In the left part of figure b, a miniature of the films created in three different holes of a metallic grid is reported.

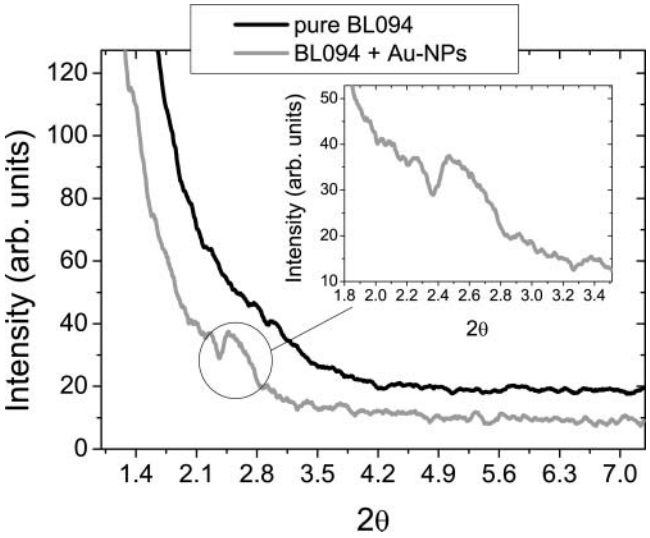

Figure 3. X-ray diffraction spectra acquired for samples of the pure BL094 (black line) and of the Au–NPs-doped BL094 (gray line).

Measurements have been done on droplets deposited on glass substrates, following the procedure described in the experimental section, for both pure and doped samples. In spectra related to the doped sample, we observed the appearance of a Bragg peak, whose spectral position corresponds to a typical smectic periodicity (3–4 nm).

The observed peak is neither intense nor sharp and it is due to the fact that we are not in presence of an aligned crystalline phase: in fact, the smectic order is limited to small domains. This is coherent with observations in Fig. 1: image of the sample acquired between parallel polarizers (a), negative of the image acquired between cross-polarizers (b) are reported. By comparing the two figures, we can notice that nanoparticle chain aggregates (clearly visible in Fig. 1(a)) are located in the defects-line surrounding uniformly aligned smectic domains, that correspond to regions of the same color in Fig. 1(b). We can conclude that gold NPs and their aggregates, formed during the thermal cycle, play an important role in the new liquid crystal configuration by inducing a higher order at the mesoscale.

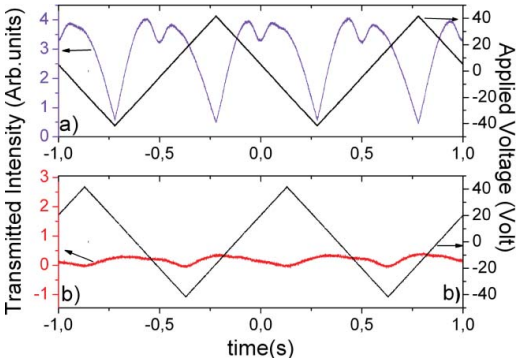

Figure 4. Electro-optical response of the pure a Au–NPs-doped BL094 confined in a planar cell.

The change in the liquid crystal order has an effect on macroscopic properties of samples.

In Fig. 4, we reported the comparison between the electro-optical response of Au–NPs-doped BL094 (a) and pure of BL094 (b) confined in planar cells, when a triangular voltage is applied to the samples.

The response of the two samples results quantitatively different. The pure cholesteric does not feel the effect of the field till a threshold voltage of 20 V. The doped sample instead starts to feel the effect of the applied field at much lower threshold value ($\approx$ 3 V). Nevertheless, the smectic domains present in the doped sample are randomly oriented in space and this lack of organization has a consequence in the macroscopic electro-optical

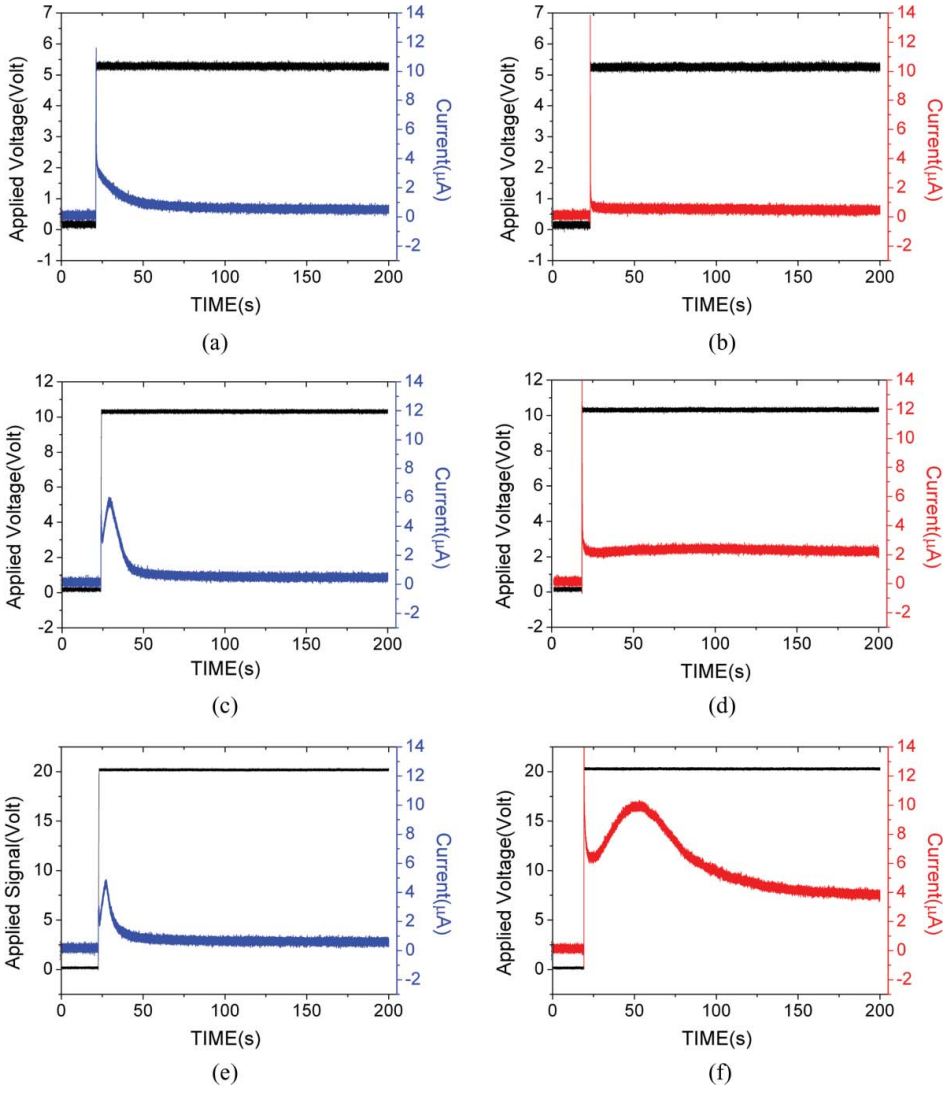

Figure 5. Current signal measured for pure (a-c-e) and doped LC (b-d-f) for different amplitudes of an applied step voltage.

response: it is just an average of different contributes and cannot reflect the order present in the single domain.

Electric Properties

Besides affecting its phase, the presence of nanoparticles and their aggregates have an effect on the electric properties of the liquid crystal. Here, we report the measurements of the current flowing in the samples while a continuous field was applied to them.

In Fig. 5 are shown the graphs related to the response of the samples to different applied voltages of a step function.

After each measurement, the sample has been refreshed by applying a continuous field with opposite sign. For the pure LC, (Fig. 5(a)–(e) large part of the charge is transferred in the first 50s (35%–48%) and the total charge transferred (Q) is slightly increasing with the value of the applied field. Q evaluated for graph 5 (a-c-e) is, respectively, 143, 153, and 155 μC.

The Au–NPs-doped LC instead (Fig. 5(b)–(f)) exhibits a threshold behavior: with a small total transferred charge when 5 V are applied (90 μC) and with a total charge of 454 μC and 1 mC while, respectively, 10 and 20 V are applied. Moreover, in Fig. 5(a) large current bump appears, with a maximum value of current for $t = 50$ s. In the measurements related to just BL094, the charge carriers are identified with the impurities present in the pure liquid crystal.

For the lowest voltage applied to the doped samples, these impurities are still the main player of the process. Below the threshold, the flows of impurities across the sample are inhibited by NPs presence. This has been confirmed by an impedance spectroscopy analysis, that we will not report here for brevity but that is discussed in details in reference [16]. The ion conductivity evaluated for doped LC results three times smaller than in pure LC.

When higher voltages are applied (10 and 20 V), the transferred charge increases significantly. We hypothesize that when the applied field is strong enough, citrate ions forming nanoparticles capping are stripped off, becoming available to be transported through the cell, generating an increase of the measured current. The other hypothesis is that NPs itself, being surrounded by charge particles, above a certain value of the field are able to move generating the additional current detected.

Conclusions

In conclusion, noble metal nanoparticles dispersed in chiral liquid crystal phases induce a striking modification of LC structural ordering accompanied by electric properties changes. Optical and structural investigation techniques have evidenced the occurrence of coexisting smectic-like phases. This is a remarkable result considering that the bulk phase sequence of this thermotropic liquid crystal does not comprehend any smectic phase. Current measurements evidenced a threshold behavior: for low applied voltages nanoparticles inhibits impurities motion across the samples, while for higher voltages nanoparticles itself are able to participate to the charge motion mechanism. These results suggest interesting scenarios where LC reconfigurability can be exploited to create plasmonic soft composite matrices.

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