Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

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To cite this article: Giovanna Palermo, Luciano De Sio, Tiziana Placido, Roberto Comparelli, Maria Lucia Curri, Roberto Bartolino & Cesare Umeton (2015) Plasmonic Thermometer Based on Thermotropic Liquid Crystals, Molecular Crystals and Liquid Crystals, 614:1, 93-99, DOI: 10.1080/15421406.2015.1050279

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1050279

Published online: 18 Aug 2015.

Mol. Cryst. Liq. Cryst., Vol. 614: pp. 93–99, 2015

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2015.1050279

Plasmonic Thermometer Based on Thermotropic Liquid Crystals

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Localized plasmon resonance (LPR) of noble Metal Nanoparticles (MNPs) opens up a new horizon for nanoscale materials able to convert light into heat, since the strong electric field generated around the MNPs can transform them into original heat nanosources. Thus, investigation of the heat transport mechanism, from the heated MNPs to their surrounding medium, is fundamental for realizing applications in nanotechnology and thermal-based therapies, and a challenge is definitely represented by the possibility of measuring temperature variations at the surface of the MNPs undergoing optical illumination. In this framework, we show that an ingenious combination of characteristics of short pitch liquid crystalline compounds and MNPs has demonstrated effective to provide an advanced tool to monitor nanoscale temperature variations.

Keywords Cholesteric Liquid Crystals; Temperature; Gold nanorods; selective reflection band; nanoscale thermometer

Introduction

One among the oldest and fascinating applications in plasmonics dates back to the Lycurgus cup, which is also one of the first historical examples of use of nanomaterials. In this cup, its matt green color changes into an intense red when the light passes through the glass wall of the cup. Such a phenomenon relies on the presence of a small amount of gold and silver nanoparticles (NPs), with at least one dimension less than 100 nm, embedded in the glass [1]. Metal NPs are characterized by Localized Plasmon Resonance (LPR), that is a strong

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absorption which takes place when a light beam with a specific wavelength impinges on them, leading to an oscillation of the conduction band electrons, which is coherent with the electric field of the incident light [2].

The same characteristics, while only empirically exploited in the Lycurgus cup, have been much later purposely designed in metallic nanomaterials, obtained with advanced synthetic techniques, potentially turning in an impressive technological impact. To date, synthetic routes enabling utilization of metal NPs with tailored shape and size offer a powerful tool to control LPR of NPs [3]. The spectroscopic properties of NPs, indeed, can be described in the framework of Mie (Equation 1) and Gans (Equation 2) theories, implemented to explain the behavior of spherical and rod like NPs, respectively. According to these models, the absorption and scattering processes for very small colloidal particles can be described by considering the extinction cross section, which depends on the wavelength λ of the impinging light, on the volume V of the NPs and on the dielectric function of the metal:

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

$$\sigma_{ext} = \frac{2\pi V}{3\lambda}\varepsilon_m^{3/2}\sum_{j=a,b,c}\frac{\left(1/P_j^2\right)\varepsilon_2}{\left[\varepsilon_1+\left(1-P_j\right)\varepsilon_m/P_j\right]^2+\varepsilon_2^2} \tag{2}$$

In (1) and (2), both the real and imaginary parts of the dielectric function of the metal (ε_1 and ε_2, respectively) appear, along with the dielectric function of the surrounding medium ε_m [4], being this last a key player for realizing active plasmonic devices [4], while P_j indicates depolarization factors.

The properties of Au NPs, relevant for the fundamental understanding of processes at nanoscale, can be exploited for a wide range of applications, spanning from photonics [5] to biomedicine [6] and renewable energy [7]. In this work, the attention is focused on the possible use of Au NPs in cancer therapy. Plasmonic Photothermal Therapy (PPTT) represents a drug free cancer treatment, based on the utilization of Au NPs to destroy cancer

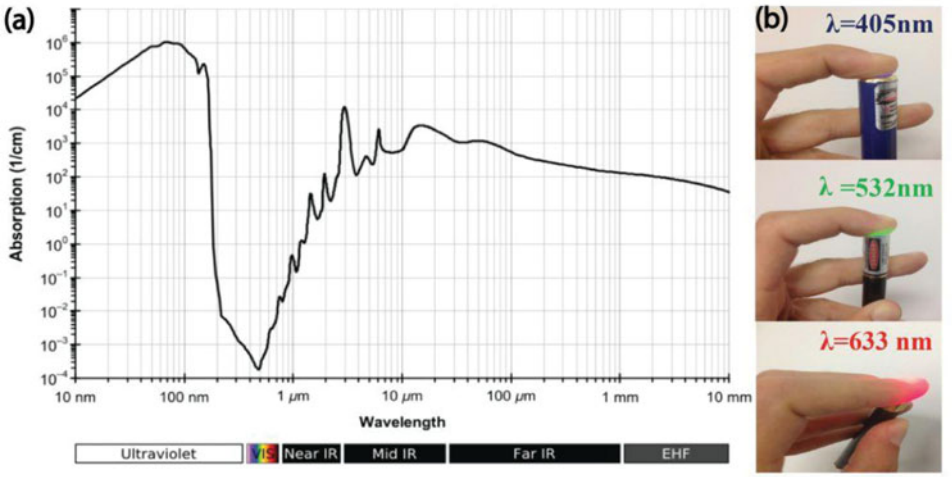

Figure 1. Liquid water absorption spectrum **(a)**; Penetration of visible light into living tissue **(b)**.

cells in a selective way, without affecting the healthy tissue. For this purpose, it is important to minimize the heat of the healthy tissue, a task that can be accomplished by exploiting the extraordinary capability of NPs to convert light into heat, when shed through a biological window[8]. To this aim, it is necessary to work with an infrared radiation, whose wavelength perfectly falls in the so called "first water window", where the absorption of the human tissue is minimum (Fig. 1a).

In fact, by observing the penetration into a human finger of visible light of three different wavelengths, it is evident that, moving toward the infrared region of the spectrum, the penetration depth noticeably increases (Fig. 1b). In addition, in presence of NPs, light scattering is drastically reduced in the wavelength range of the plasmonic band of NPs, in favor of a higher absorption. This remarkable capability of NPs to generate localized heat represents a powerful tool; however in order to effectively exploit such a potential, an extreme accuracy in determining temperature variations in the vicinity of NPs is required.

Here we present an original method to monitor the heat generated at the nanoscale by using Gold Nanorods (GNRs), that are NPs which, due to their asymmetric shape, possess two LPRs: a transverse and a longitudinal one. Remarkably, acting on the GNRs aspect ratio, the position of their longitudinal LPR, which shows a high sensitivity towards the surrounding medium, can be finely tuned in the visible and near infrared range [3]. For our purpose, a smart thermosensitive material (Cholesteric Liquid Crystal - CLC [9]), which is able to change its selective reflection band as a function of temperature, has been specifically selected to measure temperature variations around the NPs of our sample. By recording the spectrum of the mixture CLC – GNRs for different values of the temperature around the NPs, in which the longitudinal LPR has been suitably excited, we have made a calibration of our nano-thermometer, which enables an estimate of the induced temperature variations.

Materials and Method

Water dispersible, cetyltrimethylammonium bromide (CTAB) capped, GNRs have been synthesized by suitably modifying a previously reported, seed mediated, protocol involving a room temperature chemical reduction of $HAuCl_4 \cdot 3H_2O$ in a CTAB micellar solution, assisted by $AgNO_3$, to promote an anisotropic growth [13]. GNRs have been subsequently transferred in chloroform by functionalization with decanoic acid, as already reported

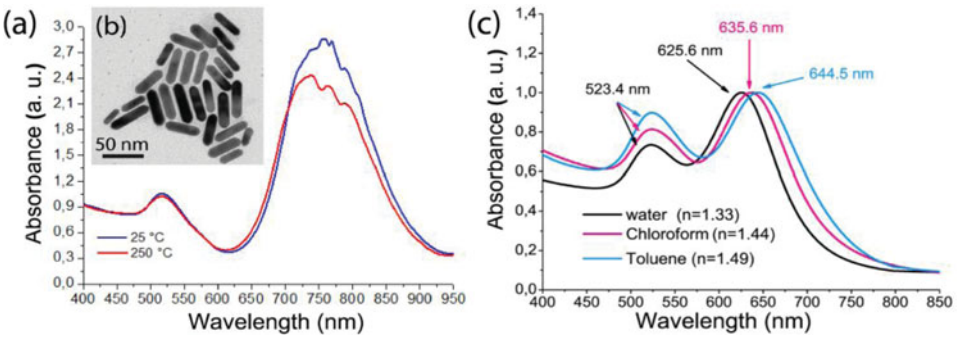

Figure 2. Thermal stability test of GNRs dispersed in chloroform **(a)**; TEM micrograph of the GNRs dispersed in chloroform **(b)**; normalized absorption spectra of GNRs in different dispersing media **(c)**.

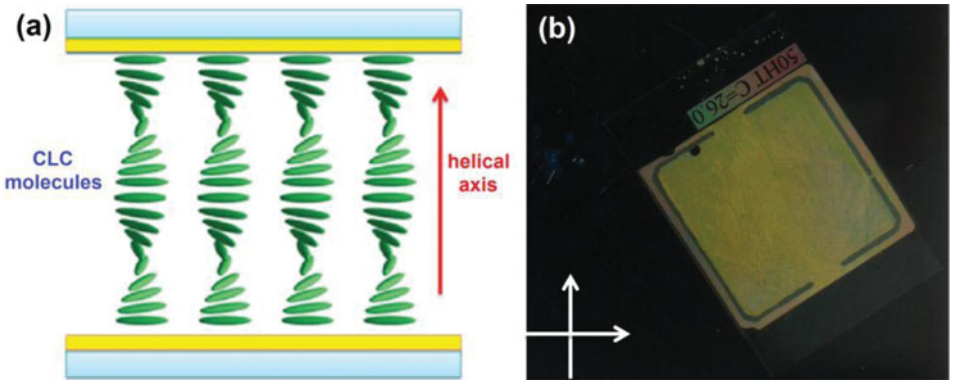

Figure 3. Sketch of a planar alignment of Cholesteric Liquid Crystal in a cell **(a)**. Polarized optical microscope view of the CLC-GNRs sample **(b)**.

elsewhere [13], in order to become dispersible in a common medium with Liquid Crystals (LCs).

The stability of GNRs in chloroform has been tested by heating the dispersion of GNRs up to 250°C. Remarkably, we have observed that, up to 100°C, GNRs do not exhibit any modification induced by the thermal treatment, thus confirming that they preserve their geometry. Moreover, by heating the solution up to 250°C, we have observed (Fig. 2a) an irreversible modification (in terms of width and amplitude) of the longitudinal plasmon band, which is due to a change of the GNRs shape (the so called reshaping) [14]. Furthermore, the Transmission Electronic Microscope (TEM) image reported in the inset of Fig. 2a shows that the main GNRs population presents an aspect ratio (AR) of 2.3, and no variation in the AR is detected upon the thermal treatment. The transfer of the GNRs in a different dispersing medium, chloroform and toluene, has been found to induce a shift of the longitudinal plasmon band, (Fig. 2c), which can be explained by taking into account the high sensitivity of the extinction coefficient of the system to the actual value of the refractive index of the surrounding medium [15].

In fact, under resonance conditions, the heat product by the NPs, due to the Joule effect, is directly proportional to the energy of the strong electric field generated around the NPs [12]. Indeed, as shown by Eq. (3), the heat generated is proportional to the square of the electric field inside the NPs E_{int}, which is, in turn, directly proportional to the external electric field E_0 [Eq. (4)]. Therefore, the heat generated around the NPs results directly proportional to the intensity of the impinging light.

$$q(r) = \frac{\omega}{2} \mathrm{Im}\left(\varepsilon(\omega)\right) \varepsilon_0 \left|E_{\mathrm{int}}(r)\right|^2 \tag{3}$$

$$E_{\mathrm{int}} = \frac{3\varepsilon_m}{\varepsilon(\omega) + 2\varepsilon_m} E_0 \tag{4}$$

In order to exploit the possibility of using NPs as nano-source of heat [13], the possibility of monitoring temperature variation in their vicinity under optical illumination is crucial. For this purpose, a clever combination of NPs with a thermosensitive materials has been studied.

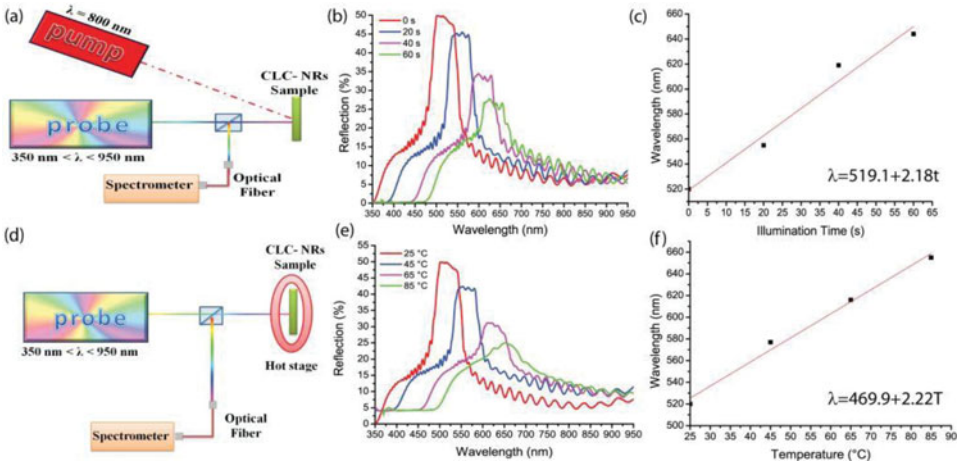

Figure 4. Pump-probe setup **(a)**; Reflection response of the CLC-GNRs sample under optical pumping **(b)**; Linear fit of the position of Bragg's wavelength versus illumination time **(c)**; Thermal setup **(d)**; Reflection response of the CLC-GNRs sample under the temperature variation effect **(e)**; Linear fit of the position of Bragg's wavelength versus temperature **(f)**.

Namely, GNRs have been dispersed in a thermotropic liquid crystal, which is able to change its optical properties as a function of external perturbations, such as electric or magnetic fields, and temperature variations [16]. In particular, it has been selected a cholesteric liquid crystal (CLC) that behaves as a one dimensional photonic band gap, due to the periodic arrangement of its molecules; in this way, a specific wavelength can be reflected (Bragg's wavelength) once the CLC is aligned in a planar geometry inside the cell (Fig. 3a).

In order to detect temperature variations around GNRs, the ability of CLC to tune its reflection band as a function of these variations has been exploited. The utilized CLC is characterized by a Bragg's wavelength $\lambda_B \approx 0$ nm and has been obtained by twisting a nematic LC (MDA-00–1444, by Licristal) with a 20% in weight of a chiral agent of (ZLI-811, by Licristal); then, a homogeneous mixture with GNRs (up to 7 wt%) has been prepared. The presence of GNRs in the system has been found to red-shift the typical reflection band of the CLC; however, this shift can be eliminated by adding a given amount (8%) of chiral agent to the mixture; in this way, the Bragg's wavelength of the CLC-GNRs sample turns out to return around 520 nm. By capillary flow, the mixture was then introduced at room temperature in a cell, whose glasses were treated to obtain a planar alignment of the CLC. In this way, the CLC director "**n**" orients parallel to the substrates, while its helical axis goes normal to them (Fig. 3a). In Fig. 3b it is possible to see the sample between crossed polarizers, which appears bright due to its birefringence.

Optical Characterization

To investigate the influence on the CLC configuration of the local heating induced by a suitable optical radiation through the GNRs resonance, we have performed all-optical experiments by means of the pump-probe setup reported in Fig. 4a. This utilizes a collimated white source (350 nm $< \lambda <$ 950 nm) for monitoring the spectral properties of the CLC configuration, and a CW NIR pump laser emitting at $\lambda = 800$ nm (power pump

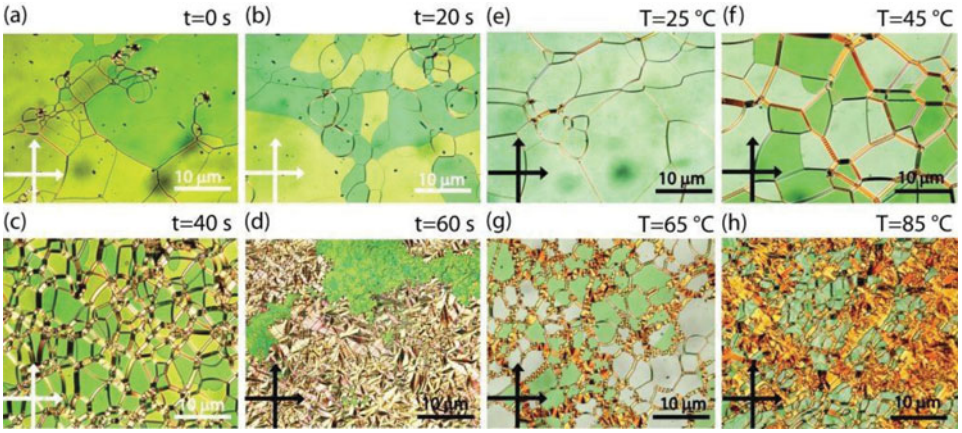

Figure 5. POM view of CLC-GNRs sample between crossed polarizers for different illumination time: 0 s **(a);** 20 s **(b);** 40 s **(c);** 60 s **(d);** and value of temperature: 25°C **(e);** 45°C **(f)**; 65°C **(g)**; 85°C **(h)**.

$P = 0.2\ W/cm^2$), corresponding to the longitudinal band of GNRs. The reflection component of the sample has been monitored by means of a spectrometer Ocean Optics (USB2000+).

Fig. 4b reports the behavior of the sample (CLC-GNRs) under illumination with the pump beam, for different exposure times. The CLC acts as a mirror for wavelengths of the impinging white light falling within the reflection band, which are back reflected. By optically pumping a given sample area, the photoexcitation of GNRs induces, due to the Joule effect, a generation of localized heat, which induces an elongation of the CLC pitch, with a consequent linear red-shift of the reflection band. Indeed, by keeping constant the pump power and increasing the exposure time, a linear red shift and a partial suppression of the reflection band are detected, which are due to a gradual increasing of the local temperature. In addition, the elongation of the CLC pitch reduces the number of periods in the bulk of the cell, an effect that yields an attenuation and a broadening of the reflected signal amplitude.

To validate the effect of the GNRs-induced local heating on the CLC optical response, a control experiment has been performed by increasing the sample temperature from 25°C up to 85°C by means of a hot stage (Fig. 4d) and monitoring the behavior of the reflected signal (Fig 4e). Also in this case, a linear red-shift has been observed, which clearly confirms the photo-thermal behavior reported in Figure 4b.

The sample morphology has been investigated by means of a Polarized Optical Microscope (POM): Figs. 5(a–d) and Figs. 5(e–h) show that, by heating up the sample both with light and uniform heating, it is possible to induce drastic morphological changes in the sample textures (the so called oily streaks), which reflect the correlation between the position of the reflection band and the temperature of the sample.

The fact that our system can be utilized for monitoring temperature variations, occurring in the sample under optical illumination, is confirmed by the circumstance that the two functions reported in Figures 4c and 4f, which fit the position of Bragg's wavelength as a function of the illumination time and as a function of temperature, respectively, exhibit, within the experimental error, the same linear behavior. This represents a clear confirmation that the photoexcitation of the NPs in the sample produces the same spectral effects produced by temperature variations induced by the hot stage. The thermal sensitivity of the proposed method has been evaluated by means of the linear fit used to obtain the relation between

temperature (T), and Bragg's wavelength (λ_B):

$$T = \frac{1}{2.28}\lambda - 206.09 \tag{5}$$

For the measured values and precision of λ_B, by using the error propagation, we obtain:

$$\Delta T = 0.35^{\circ}\mathrm{C} \tag{6}$$

which shows that temperature in the vicinity of GNRs can be measured with a quite high accuracy.

Conclusions

We present a method showing that it is possible to exploit the properties of soft matter to carry out an accurate evaluation of temperature variations. Thanks to the periodic arrangement of the director in a CLC, and to its sensitivity to temperature variations, is possible to monitor the temperature around NPs in a mixture of CLC-GNRs. In this way, by simply acquiring the spectrum of the sample, it is possible to estimate temperature variations around NPs with the quite high sensitivity of about 0.35°C.

Funding

The research is supported by the Air Force Office of Scientific Research (AFOSR), Air Force Research Laboratory (AFRL), U.S. Air Force, under grant FA9550-14-1-0050 (P.I. *L. De Sio*, EOARD 2014/2015) - Materials and Manufacturing Directorate, AFRL, by PRIN Anno 2010–2011 – prot. 2010C4R8M8 and by Sens&Micro LAB Project (2007-2013) funded by Apulia Region (Italy).

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