Thermo-plasmonics in self-organized nanostructured materials

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ABSTRACT

Gold nanorods embedded in cholesteric liquid crystals allow controling the selective reflection of a light beam. Investigation of morphological and optical properties of the obtained material reveals a new efficient tool to detect temperature variations at the nanoscale.

Keywords: nanomaterials, plasmonics, liquid crystals, heat transfer, nanomedicine.

1 INTRODUCTION

Plasmonic nanoparticles (NPs) have a significant potential as key components in miniaturized all-optical computing nanocircuits due to their capability of confining light at the nanoscale beyond the so called diffraction limit of light by exploiting Localized Plasmonic Resonance (LPR) [1]. Such NPs have also a large technological impact in sensing and energy-harvesting applications as well as in medical domains, as active elements in photothermal therapy [2]. Indeed, due to the electron-electron collisions, the localized electric field generated around the NPs is converted to heat and the NPs behave as nano-sources of heat. At the same time, an important challenge is represented by the ability of measuring temperature variation at the surface of the NPs under optical illumination, since nano-localized temperature variation is the most important parameter for applications ranging from nanomedicine to photonics. A particular class of metal NPs is represented by gold nanorods (GNRs) which have two LPRs, transverse and longitudinal, the second one tuneable from visible to NIR as a function of particle geometry. Investigation of the heat transport mechanism, from the irradiated GNRs to their surrounding medium, is a fundamental step in realizing nano-localized sources of heat for applications in nanotechnology and thermal-based therapies. We made a breakthrough in the monitoring of nanoscale temperature variations under optical illumination by combining GNRs properties and thermosensitive materials. Compared to previously reported techniques [3] the proposed method offers an innovative non-invasive tool able to address the properties of well known materials, like Liquid Crystals (LCs) for monitoring photoinduced temperature variations around GNRs with high sensitivity.

2 SYNTHESIS OF GOLD NANORODS

2.1 General Protocol for seed-mediated synthesis of GNRs

Water-dispersible GNRs were synthesized by means of a seed mediated protocol [4]. The first step involves the preparation of gold "seeds" (GNPs with diameter <3.5 nm) by reducing $HAuCl_4$ (5×10^{-4}M) with $NaBH_4$ (0.01M) in presence of CTAB (0.2 M). The seed solution was kept for 2 h under stirring. In the meanwhile the so-called "growth solution" was prepared mixing $HAuCl_4$ (0.024M), CTAB (0.08 M), the proper amount of cyclohexane and acetone, and $AgNO_3$ ([Au]/[Ag] = 20). Au(III) was reduced to Au(I) by addiction of ascorbic acid ([ascorbic acid]/[Au^{3+}] = 2) obtaining a colorless solution. At this stage the growth of GNRs was triggered by addition of "seeds" solution. The turning of the solution color to blue indicates the formation of anisotropic particles (Figure 1a). The samples were purified from excess of surfactant by centrifugation cycles and were optically and morphologically characterized.

2.2 Phase transfer of GNRs from water to organic solvent

Water-dispersed GNRs were transferred in chloroform or toluene by functionalization with decanoic acid [5]. Briefly, the GNRs water solution was mixed with 100 mg of decanoic acid and shaken, then neat chloroform (or toluene) was added to such GNRs solution. Finally, the carbonate

buffer (pH=9.6) was added and the mixture was shaken thus promoting the quantitative phase transfer in chloroform or toluene. (Figure 1b)
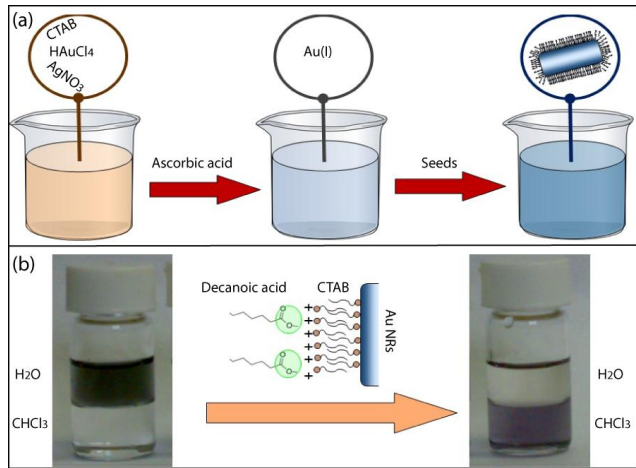

Figure 1: Schematization of the (a) synthesis process of GNRs and (b) their phase transfer from water to organic phase

2.3 Optical properties of GNRs

Normalized UV-Vis absorption spectra of GNRs dispersed in different solvents are shown in Figure 2a. The GNRs dispersion exhibits two typical plasmon bands: a transverse one at 523 nm and a longitudinal one at 625 nm (Figure 2a, black line). The spectral features of GNRs are retained if transferred in the chloroform or toluene phase, although the peak wavelength of the longitudinal band is red-shifted with respect to that one in water. This behaviour can be explained by taking into account that for ellipsoidal particles, as predicted by Gans theory [6] the spectral position of the LPR peak depends on the refractive index of dielectric material surrounding the GNRs.
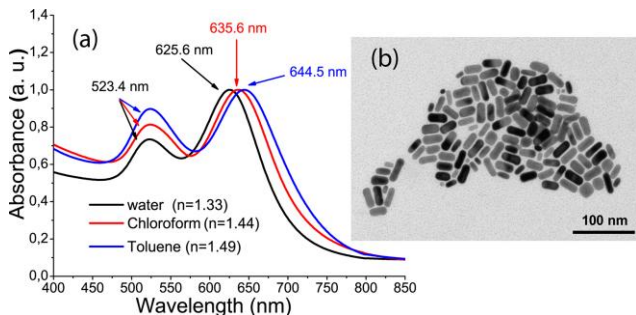

Figure 2: Normalized UV-Vis absorption spectra (a) for water (black line), chloroform (red line) and toluene (blue line) dispersions of GNRs. TEM image the chloroform dispersed GNRs (b)

Here, as the refractive index of the surrounding medium turns from 1.33 (water) to 1.44 (chloroform) or 1,49

(toluene) the longitudinal plasmon band of GNRs solution is red-shifted of about 20 nm (Figure 2a, red and blue lines) with respect to the aqueous solution of GNRs (Figure 2a, black line). Note that, due to its low sensitivity to change in refractive index of the surrounding medium, the transverse band (524 nm) does not exhibit any shift against the high sensitivity of the longitudinal plasmon band. The Transmission Electron Microscopy (TEM) image obtained by depositing one droplet of chloroform GNRs dispersion onto a carbon-coated copper grid, shown in Figure 2b, indicates that the transfer in organic solvent does not induce any change in shape and size of particles. The particle population consists mainly of GNRs with 2.5 ± 0.4 aspect ratio.

3 CHOLESTERIC LIQUID CRYSTALS

Thermotropic Cholesteric Liquid Crystals (CLCs) are short pitch (P) chiral materials that organize in layers with no positional ordering of the molecules within the layers, but exhibiting a mesoscopic order described by a helicoidal orientation of the director axis from layer to layer. CLCs aligned in a Grandjean texture (that means CLC helices oriented perpendicular to cell surface, see schematic in Figure 3a) behave as one-dimensional photonic band gap systems where propagation of light of given wavelengths and polarization states is forbidden [7]. It is well known that a circularly polarized light of the same handedness as the CLC helix and having wavelength between $n_o P$ and $n_e P$ (n_o and n_e being the ordinary and extraordinary refractive indices of the material, respectively), at normal incidence on a CLC system in a planar configuration (helix axis perpendicular to the plane of the cell), is reflected (red curve, Figure 3a) by the CLC layer, while light of the opposite handedness (blue curve, Figure 3a)) propagates unaffected through the CLC. For unpolarized light in the wavelength range $n_o P < \lambda < n_e P$, an ideal sample reflects 50% of the impinging intensity and transmits the remaining 50%, whereas the sample remains transparent to light with wavelength outside that range. Relationships between the reflected Bragg wavelength (λ_B), the bandwidth ($\Delta\lambda$) and P of a CLC reflection band are shown in Equations 1, 2 and 3:

$$\lambda_B = \bar{n}.P \qquad (1)$$
$$\Delta\lambda = \Delta n.P \qquad (2)$$
$$P = 1/HTP[C] \qquad (3)$$

where $\bar{n}$ is the average refractive index of the mixture, Δn is its birefringence, HTP is the helical twisting power of the chiral dopant and $[C]$ is its concentration. Figure 3c is a Polarized Optical Microscope (POM) photo of the sample where the presence of disclinations is evident. In fact, in a flat cell with layers parallel to the bounding plates, this kind of structural defects, called "oily streaks", appear as long bands that divide the ideal domains of the layers; the inner structure of domains is quite complicated and depends on

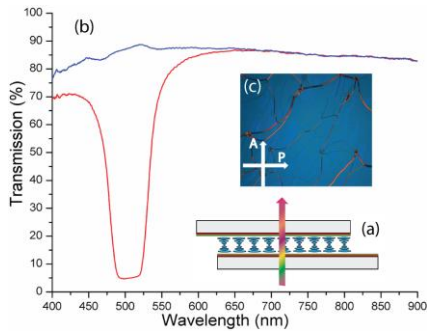many parameters, such as CLC elastic constants, surface anchoring and cell thickness.

Figure 3: Sketch of the CLC director configuration in the aligning cell (a) along with a spectral response of the sample (b) for light left (red) and right (blue) circularly polarized. (c) POM view of the sample.

3.1 CLC hosting GNRs

In order to study the influence of GNRs on the CLC (BL095 by Merck) textures, we have realized homogeneous mixtures of short pitch (≈ 400nm) CLC with different concentrations of chloroform disperisons of GNRs, up to 10% in weight. Glass cells of 20μm thick gap treated with a thin polyimide layer where induction of a preferred planar LC direction was obtained via rubbing, have been then filled at room temperature by capillary action.
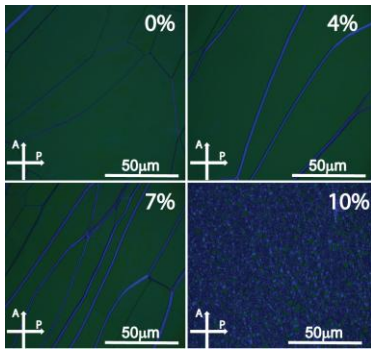

Figure 4: POM view of samples with different GNRs concentrations.

Figure 4 is a POM view of samples with different GNRs concentrations: It is evident that the CLC textures are affected by the presence of GNRs. In details, for low concentration (0-4%) the GNRs do not induce a noticeable variation on the oily streaks of the CLC. On the contrary, above this value, GNRs affect the elastic properties of the CLC helical structure by deforming it and consequently inducing the formation of more defect lines. In the range 3-7% the number and the width of defect lines strongly depend on the GNRs concentration. Finally, for concentration values above 7%, the CLC phase was found to be completely destroyed, with only the classical conic

textures (marker of a random aligned CLC phase) visible (Figure 4, 10%).
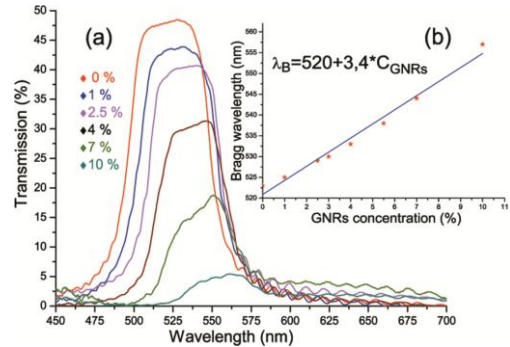

Figure 5: Reflection spectra of the sample (a) and Bragg wavelenght (b) versus the GNRs concentrations.

The reflection band of samples (for unpolarized light) with increasing GNRs concentration values (Figure 5a) were also detected. It turns out that, due to a modification of the CLC elastic properties, the system energy is minimized trough a variation/distortion of the helix pitch, which yields a lowering of the reflected intensity. Moreover, according to equation (1), due to the induced refractive index variation (since gold exhibits a higher refractive index with respect to pure CLC) the center of the reflection band is red-shifted while increasing the GNRs concentration. Up to 7% in GNRs concentration, the reflection band can be pulled back by adding a given amount (5-7%) of chiral agent (ZLI-811, by Licristal); above that value, the CLC phase is destroyed and cannot be restored.

4 PHOTO-HEATING OF GNRs

The value of the CLC pitch *P* is sensitive to all those factors (e.g. temperature) that can affect the balance of molecular interactions and the orientation of the CLC director.
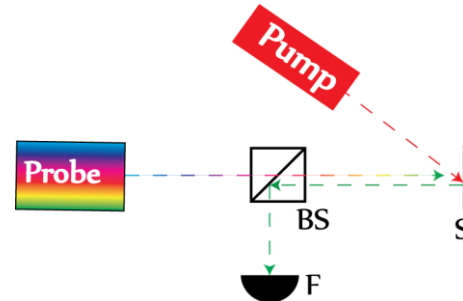

Figure 6: All-optical setup for sample characterization. BS: beam splitter; F: reflection fiber; S: sample.

In order to understand the influence on the CLC configuration of local heating induced by a suitable optical radiation through the GNR resonance, all optical experiments were performed by means of the optical setup reported in Figure 6. The setup utilizes a collimated white

source (400nm< λ<800 nm) for monitoring the spectral reflection properties of the CLC configuration, and a CW NIR pump laser emitting at λ=680 nm (P_{pump}= 0.2 W/cm^2) in the high absorption range of the GNRs (longitudinal band). The sample was probed by the white light source, monitoring its back reflected components by means of the reflection fiber (F). Figure 7 shows the behavior of the CLC reflection band under illumination with the pump beam for different exposure times. The CLC acts as a mirror for all the wavelengths within the reflection band of the impinging white light, which are back reflected. By optically pumping the same sample area, due to the electron-electron scattering and the electron-phonon coupling associated with the LPR effect, the strong electric field generated around the GNRs is converted into heat which cools rapidly by exchanging energy with the surrounding medium. This local-heating induces an elongation of the CLC with a consequent linear red-shift of the reflection band.
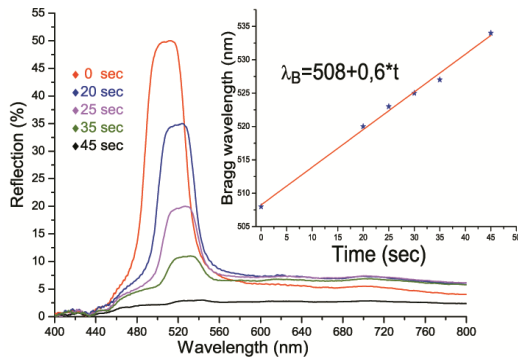

Figure 7: Reflection spectra of the sample for different values of illumination time. In the inset is reported the linear fit of the Bragg wavelenght versus the illumination time.

In Figure 7, it is easy to observe that, by keeping constant the pump power and increasing the exposure time, due to a gradual enhancement of the local temperature, a linear red shift (more than 30 nm, inset of Figure 7) and a partial suppression of the reflection band take place. Indeed, according to equation 1, the center wavelength of the reflection band is directly proportional to the pitch *P* which increases with temperature; in addition, the elongation of P reduces the number of periods in the bulk of the cell, an effect which explains the attenuation of the reflection band amplitude with temperature. To validate the effect of the GNR-induced local heating on the CLC optical response, we have performed a control experiment by varying the sample temperature from 25°C up to 65°C and monitoring the reflection band behavior; once again, we have observed a linear red-shift, which clearly confirms that the behavior reported in Figure 7 is due to a photo-thermal mechanism. The information is summarized in the calibration Table 1 which indicates in details how it is possible to obtain the temperature value around a GNR. In fact, the calibration function reported in the inset of Figures 7 (λ_B vs t) exhibits,

within the experimental error, the same linear behavior with the one obtained from table 1 (λ_B vs T; λ_B= 494+0.64*T).

Time (s)	λ_B (nm)	Temp. (°C)
0	508	25
20	517	35
25	524	45
35	529	55
45	534	65

Table1: Correlation between illumination time and temperature around the GNRs obtained by a direct measurement of the position of λ_B.

This result shows that it is possible to measure the temperature around GNRs, at a given illumination time, by simple measuring λ_B with a sensitivity of about 0.03 °C.

5 CONCLUSIONS

The realization and characterization of an innovative method for achieving optical control of the selective reflection of a CLC has been reported. A photo-thermal effect, induced by the presence of a NIR selective plasmonic resonance, can be exploited for controlling the position of the selective reflection exhibited by the CLC configuration.. This synergy between plasmonics and photonics can be used for develop a method for detecting the temperature around GNRs under optical illumination.

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