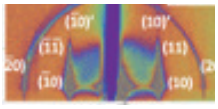

The role of topological defects in liquid crystal materials in the organization of nanoparticles

The optical properties of nanoparticles are directly related to their small size and to the electromagnetic coupling that takes place between the nanoparticles. When they are brought closer to a few nanometers, this coupling can significantly modify these properties. The community now knows how to synthesize, often in solution, a great diversity of nanoparticles, with various sizes, shapes and natures inducing the implementation of optical properties also varied. How to induce an organization of nanoparticles where the coupling between nanoparticles would be driven homogeneously to the nearest subnanometer over the entire sample from a solution of nanoparticles dispersed in a solvent? To answer this question, researchers from the INSP Physical Chemistry and Surface Dynamics team have studied the confinement of gold nanospheres in liquid crystal topological defects. They demonstrated the concentration-controlled formation of 1D (chains) or 2D (hexagonal arrays) nanoparticle networks, oriented along a single pre-defined direction on the substrate, which is otherwise difficult to achieve by other methods.

In a liquid crystal, the core of a topological defect is a disordered region that can be stabilized by incorporating a nanoparticle of the same order of magnitude. Topological defects can thus act as a trap for nanoparticles. We master the formation of smectic liquid crystal films made of arrays of two types of topological defects, 1D defects (dislocation lines) and 2D defects (grain boundaries in the form of ribbons of about 400nm width), the whole being perfectly oriented along a unique direction determined by the rubbed polymer substrate on which the liquid crystal is deposited[1].

By combining optical microscopy, Rutherford Backscattering Spectrometry (RBS), UV/visible spectroscopy and Grazing Incidence X-ray Scattering (GISAXS) on the SIXS line of the Sun synchrotron, we have determined the structure of nanoparticle organizations induced in topological defect arrays. We show that 1D defects preferentially trap nanoparticles. When the nanoparticle concentration is low, typically less than 1300 nanoparticles per µm2, nanoparticle chains are formed. The coupling between nanoparticles is then anisotropic and the absorption of incident light by the nanoparticles becomes governed by polarization. It takes place at a different wavelength depending on whether the polarization is parallel to the chains ($\lambda_{//}$ in the figure) or perpendicular ($\lambda_{\perp}$ in the figure)[2]. Confinement by 2D topological defects occurs at higher nanoparticle concentration when 1D defects are essentially filled, which is illustrated by the evolution of the anisotropy of the incident light absorption from an anisotropic absorption dominated by nanoparticle chains (low concentration in blue in the figure) to an isotropic response dominated by 2D gratings (high concentration in purple in the figure). We show by GISAXS that 2D confinement induces the formation of hexagonal arrays of nanoparticles (figure) that exceptionally turn out to be aligned along the defects, with low disorder. In both these types of organization, 1D and 2D, the nanoparticles are closer than 2nm to each other, in stronger electromagnetic coupling than when they organize in hexagonal arrays in air. Closer nanoparticles decrease the amount of disorder they can induce in the liquid crystal beyond the core of the defects[3].

1 Coursault et al., Soft Mat. 2016

2 Coursault et al. ; ACSNano 2015 ; Do et al., Frontiers 2020 ; Do et al. Nano Letters 2020

3 Do et al., Frontiers 2020 ; Do et al. Nano Letters 2020

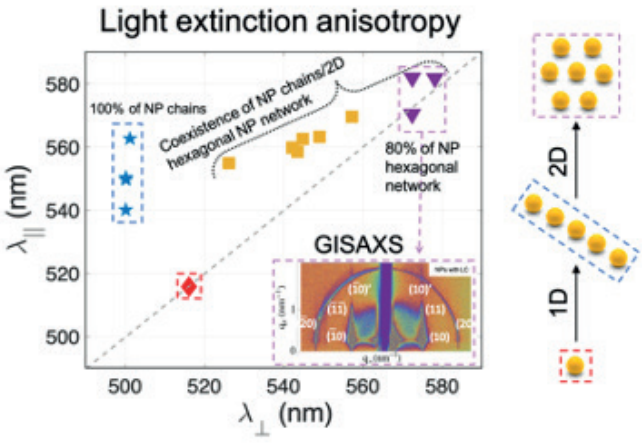

Figure 1
Evolution of the anisotropy of light absorption by gold nanoparticles (absorption wavelength for a parallel polarization as a function of the absorption wavelength for a perpendicular polarization) when the nanoparticle concentration increases. The GISAXS signal presented for the 2D ~~grating~~ in reflection geometry highlights the characteristic diffraction rods of a hexagonal 2D ~~grating~~.

We can conclude that we have at our disposal a liquid crystal matrix that can induce two types of spherical nanoparticle organizations: chains oriented in a single direction, coexisting with oriented hexagonal networks, the proportion of these two organizations being controllable by the concentration of nanoparticles. ~~It is now a question of going beyond the model system of nanospheres to~~ evolve towards more complex systems: first of all, ~~nanobatons~~ to obtain optical responses that are expected to be highly anisotropic. For metallic nanostructures the absorption could become perfectly controlled by the polarization of the incident light and for semiconduct~~or~~ nanostructures the light emission would become of fixed polarization; then mixed nanoparticle ~~systems~~ to study the interactions induced between different nanoparticles in the two types of ~~grating~~s.

Reference
"From Chains to Monolayers : Nanoparticle Assembly Driven by Smectic Topological Defects"
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