

Self-Alignment of Gold Nanorods Within Cellulose Based Liquid Crystals

Michael Campbell (Physics)

November 2nd, 2012

Committee Members

Advisor: Dr. Ivan Smalyukh (Physics)

Honors Council Representative: John Bohn (Physics)

Third Committee Member: Nathaniel Thiem (Math)

Abstract

In this work, I use cellulose nanocrystals and demonstrate the long-range bulk dispersion and self-alignment of anisotropic metal nanoparticles at well-defined orientation with respect to the far-field liquid crystal director. In the case of anisotropic plasmonic nanoparticles, the liquid crystal-mediated alignment and assembly result in a switchable polarization-sensitive plasmon resonance, different from that of the same nanoparticles in isotropic media. Polarization-sensitive absorption, scattering, and two-photon luminescence are used to characterize orientations and spatial distributions of nanorods. Effective-medium optical properties of these hybrid inorganic-organic plasmonic complex fluids match what one could expect based on entropic interactions of gold nanorods with the structured host medium of the nanocrystal-based liquid crystal. The demonstrated device-scale bulk nanoparticle self-alignment and self-assembly may enable optical metamaterial mass production and new properties arising from combining the switchable nanostructured LCs and properties of anisotropic plasmonic nanoparticles.

1 Motivation

Nanostructured composites obtained by means of self-alignment and self-assembly of nanoparticles are poised to revolutionize scientific instruments, technologies, and consumer devices. Liquid crystalline (LC) host materials may provide conceptually new means of predesigned control over large-scale self-organization of nanometer-sized particles that are not accessible in conventional isotropic hosts. A potential application of this is using self assembly to create a metamaterial. One example of a metamaterial is a material where the index of refraction is negative [8]. The index of refraction determines the amount that a light ray will bend when it enters matter. All naturally known materials have a positive index of refraction [8]. This property could eventually lead to superfine, aberration free lenses, which can resolve images smaller than the wavelength of light [8]. Another application is that light could be bent around an object, which could lead to "cloaking" an object, rendering it invisible [2].

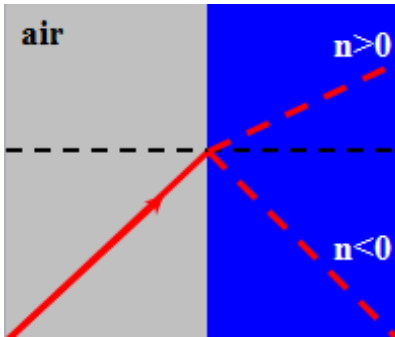


Figure 1: A material with a negative index of refraction, $n < 0$, will cause light to bend in a different direction than it would when entering a conventional naturally occurring material with $n > 1$.

Because of the new set of interesting properties, many researchers have been focused on creating nanostructured materials such as metamaterials. The research group I am working with, which is run by Dr. Ivan Smalyukh, has been investigating ways to use self-assembly to create nanostructured materials. One such system is using gold nanorods dispersed in a liquid crystal medium. The liquid crystal provides an orientational order to the gold nanorods. By achieving a dense concentration of highly ordered gold nanorods, it may be possible to create a metamaterial [4]. In this report I demonstrate that cellulose based liquid crystals can be used to provide large scale orientational order to anisotropic gold nanoparticles.

2 Introduction to Liquid Crystals

The term liquid crystal is a sort of misnomer, as a liquid crystal is neither a liquid nor a crystal; rather liquid crystals are a unique type of matter which possesses some features which are found in liquids and some features which are found in crystals[1]. Like a liquid, liquid crystals can flow, and do not break or have a solid structure[1]. Furthermore, the molecules lack three dimensional positional ordering, which is present in a crystal [1]. However, unlike a liquid, the molecules in a liquid crystal also possess some orientational order and up to two dimensions of positional order. [1] To achieve the orientational ordering, the molecules need to be anisotropic in their shape. Examples of anisotropic molecules include both disk and rod shaped molecules. Molecular shapes can also be more complicated, as is the case with the primary liquid crystal I used. [3]

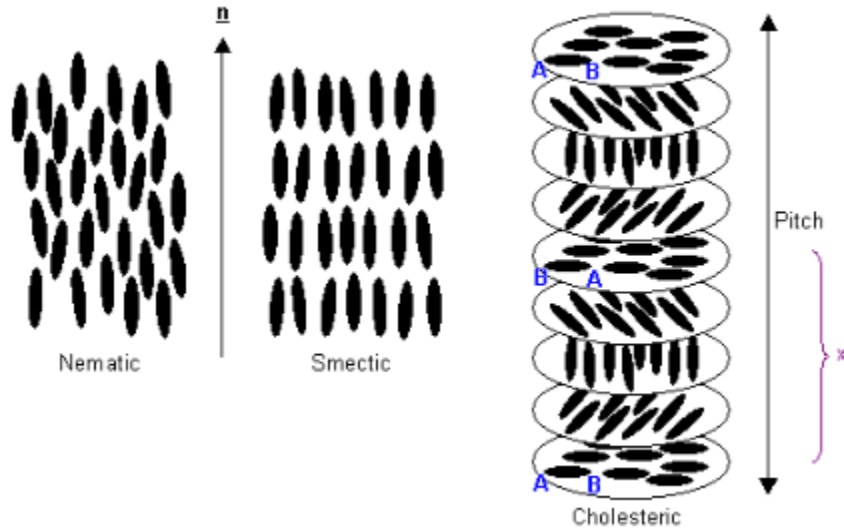


Figure 2: Three phases of a liquid crystal formed by rod like molecules. [7]

The molecules in a liquid crystal can be ordered in several different ways and the way in which the molecules are ordered is referred to as the phase. One of the most common phases is the nematic phase. If a molecule has a principle axis (for example, the long axis in a rod or the short axis in a disk), then we can define the direction of a molecule as the direction of its principle axis. In a nematic phase, all of the molecules will be aligned with an external axis, which is defined as the director, and is usually abbreviated $\vec{n}$. The director possesses a head-tail symmetry in that a state described by $\vec{n}$ is indistinguishable from a state described

by $-\vec{n}$ [1]. Because of this it is more useful to think of the director $\vec{n}$ as an axis rather than a vector.

To quantify the amount of ordering which is present within a nematic liquid crystal, we use an order parameter, called S . For a molecule with one principle axis, S is just a number. If we define θ to be the smallest angle between the director and the principle axis of a molecule, then S is given by $S = \frac{\langle 3\cos^2(\theta) - 1 \rangle}{2}$ [1], where $\langle \dots \rangle$ indicates the average over all molecules. If all of the molecules are perfectly aligned, then $S = 1$. If the molecules are aligned completely at random, then $\langle \cos^2(\theta) \rangle = 1/3$, and $S = 0$.

Within a cell, a nematic liquid crystal can align parallel to or perpendicular to the substrate. If the liquid crystal aligns parallel to the substrate, then we say the liquid crystal has planar alignment. If the liquid crystal is aligned perpendicular to the substrate, then it has homeotropic alignment.

Another important phase of liquid crystals is the chiral-nematic phase, which is also referred to as a cholesteric phase after the substance in which it was first seen[5]. A chiral-nematic phase can be visualized as several thin sheets of nematically aligned liquid crystal which are placed on top of each other in such a way that the director constantly rotates (see fig. 2). In a cholesteric phase there are two axis, the director $\vec{n}$, and the cholesteric axis $\vec{\chi}$. The director $\vec{n}$ will twist along the cholesteric axis. For example if we take z to be the cholesteric axis, then the director may be described by

$$\begin{aligned} n_x &= \cos(\theta) \\ n_y &= \sin(\theta) \\ n_z &= 0 \\ \theta &= q_0 z + \text{constant} \end{aligned}$$

Since the director has head-tail symmetry, then the material will have a period structure which repeats itself after a rotation of 180 degrees. Although the director, $\vec{n}$, has a head tail symmetry, the cholesteric axis lacks this symmetry. A cholesteric liquid crystal is distinguishable from its mirror image, which allow chiral liquid crystals to possess a handedness [1]. If a molecule has a chiral structure, such as DNA, RNA, or Tobacco Mosaic Virus, then this chiral nature can cause the molecules to form a chiral-nematic phase [5]. Rigid charged rods

will also form a chiral-nematic phase [21, 14]

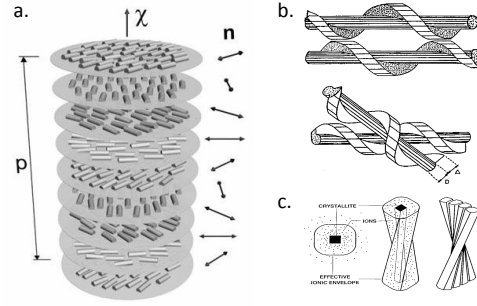


Figure 3: a. Schematic showing the alignment of molecules in a chiral-nematic phase. b. Illustration of the reduced volume that results from a chiral interaction.[6] This illustrates how a chiral nematic phase can form from chiral molecules. c. Illustration of how an electrostatic double layer of a twisted rod will also have a twist. This will lead to a twist over large distances.[6] Images b and c taken from [6]

There are two primary types of liquid crystals which correspond to distinct transitions from liquid to solid. If a liquid crystal is a substance which is dissolved in a solvent, and its concentration determines whether it is a liquid, a liquid crystal, or a solid, then it is referred to as lyotropic [1]. On the other hand, if the liquid crystal is a substance whose phase depends on temperature, then the liquid crystal is referred to as thermotropic. [1] These are not complete descriptions since a lyotropic liquid crystals behavior will depend slightly on temperature, and a thermotropic liquid crystal will also respond to changes in concentration; however, within the broad class of liquid crystals, this provides a reasonable distinction. The liquid crystal I work with, nanocrystalline cellulose, is a lyotropic liquid crystal which has a very weak response to temperature.

3 Optical Characterization of Liquid Crystals

3.0.1 Nematics

When light travels through a medium, its speed decreases according to the equation $c' = c/n$ [9], where n is the index of refraction. Nematic liquid crystals are birefringent, which means that there are two indices of refraction, one corresponding to the optical axis (which is defined to be parallel to the director), and one corresponding to a plane which is perpendicular to

the optical axis[1]. If uniformly polarized light enters a liquid crystal, with its polarization at angle θ to the optical axis, we can view the beam as two beams, one of which is polarized parallel to the optical axis, and another which is polarized perpendicular to the optical axis. If n_1 (n_2) represents the index of refraction parallel (perpendicular) to the optical axis, then the beam which is polarized parallel to the optical axis will move at speed $c'_1 = \frac{c}{n_1}$, while the beam which is polarized perpendicular to the optical axis will move at speed $c'_2 = \frac{c}{n_2}$. If a light ray is initially described by

$$E = E_0 \cos(\theta) e^{i(kz - \omega t)} \hat{x} + E_0 \sin(\theta) e^{i(kz - \omega t)} \hat{y},$$

then after the ray has traveled through the medium, it will be described by

$$E = E_0 \cos(\theta) e^{i(kz + kdn_1 - \omega t)} \hat{x} + E_0 \sin(\theta) e^{i(kz + kdn_2 - \omega t)} \hat{y},$$

where d is the distance across the sample. The waves here will now be out of phase, which will cause the polarization to rotate.

This rotation allows us to see the order of liquid crystals. In a nematic phase, when a light ray is polarized along the optical axis of the liquid crystal, its polarization will not rotate upon entering the sample. Thus after the ray has passes through the sample, it will have no component perpendicular the optical axis. Similarly when a light ray is polarized perpendicular to the optical axis, its polarization will not rotate as it passes through the sample. If we use a microscope with two polarizers, one which polarizes the incoming light (called the polarizer), and the second which polarizes the outgoing light (referred to as the analyzer), then the transmission without a sample will be zero. However, if we put a liquid crystal between the two polarizers, the light ray will rotate in the sample, and some light will then pass through the analyzer. The intensity of light, I , which passes trough to the analyzer is given by the equation [10]

$$I = I_0 \sin^2(2\theta) \sin^2\left(\frac{\pi \Delta n d}{\lambda}\right)$$

where $\Delta n = n_1 - n_2$, d is the thickness of the sample, I_0 is the original intensity of light, θ

is the angle between the polarization of light and the polarizer, and λ is the wavelength of light. Thus by viewing a sample under cross polarized light, and rotating it, we can detect whether the sample possesses orientational order.

While this method can tell us whether a sample has orientational order, it does not tell us which way the molecules are aligned since the intensity of light is periodic and repeats itself every 90 degrees. However if we wish to know the orientational order within a liquid crystal, we can use a quarter wave plate placed in between the sample and the analyzer. The quarter waveplate is a birefringent plate that retards one wave by a quarter of its wavelength, which converts linearly polarized light into right handed circularly polarized light [10]. By measuring the optical properties resulting from the addition or subtraction of the phase retardation due to the wave plate, it is possible to determine the orientation and birefringence (Δn) of a sample [10].

3.0.2 Cholesterics

There are two methods we used to observe a cholesteric structure. The first was using cross polarized microscopy, which can observe a cholesteric structure with a cholesteric axis which is parallel to the substrate. In this case, the liquid crystal will have homeotropic alignment in some regions, and planar alignment in other regions. In the region of homeotropic alignment, there is only one axis, so there is no birefringence; in the region of planar alignment, the birefringence is maximized. Thus the liquid crystal will have alternating bright and dark stripes. The distance between bright stripes is equal to half of the pitch. This characteristic structure which is observed is often referred to as the fingerprint pattern.

This form of microscopy can only be used to characterize cholesterics with large pitches. When cellulose dries, it can form a pitch which is on the order of the wavelength of visible light [24]. To characterize pitches which are on the order of the wavelength of visible light, we can use Bragg reflection. We can approximate the index of refraction as the average index of refraction (n') and a small periodic term, which reflects the periodic chiral-nematic alignment of the molecules. Since the index of refraction varies periodically, it will have a Bragg reflection when the wavelength of light is an integer multiple of the pitch of the substance. In the substance, the wavelength of light is approximately given by λ/n' , where λ

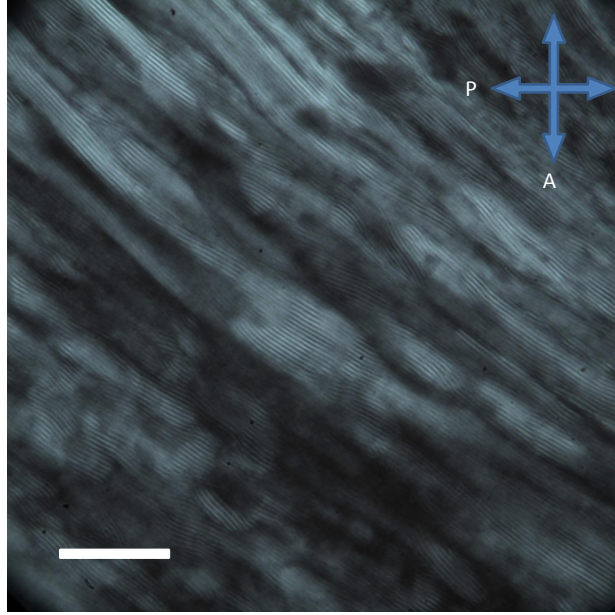


Figure 4: Cholesteric phase of cellulose nanocrystals taken under cross polarized microscopy, notice the characteristic fingerprint texture, the scale bar is 50 microns.

is the wavelength in vacuum. Thus the structure will give a Bragg refraction at wavelengths of

$$\lambda = mn'P,$$

where m is an integer and P is the pitch.

4 Plasmon Resonance

A localized surface plasmon is defined to be a nonpropagating excitation of the conduction electrons of a metallic nanostructure coupled to an electromagnetic field[16]. In my research, I use gold nanoparticles which are much smaller than the wavelength of light. Since they are smaller than the wavelength of light, a lightwave interacting with a gold nanorod is equivalent to a time dependent electric field, $E(t) = E_0 \cos(\omega t)$, interacting with the nanoparticle. The electrons in the gold nanoparticle also have a fundamental frequency which they can vibrate at. Thus when the frequency of light is similar to the resonance frequency of the electrons in the gold nanorods there will be a resonance, and consequently, light at this frequency will be absorbed by the nanoparticles. This resonance is referred to as the surface plasmon

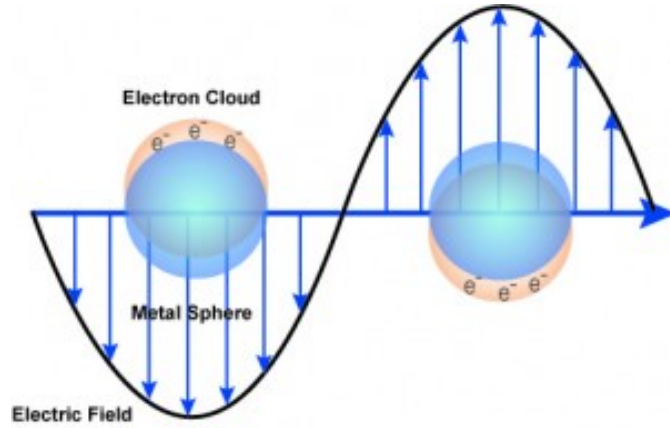


Figure 5: A gold nanoparticle under an electric field of an optical wave with a wavelength which is larger than the particle size. [15]

resonance, (SPR)[16].

A gold nanorod can have two plasmon resonances, one corresponding to oscillations of the conduction electrons along the long axis, and another corresponding to oscillations of the conduction electrons along the short axis[16]. With the gold nanorods we used, the short axis had a surface plasmon resonance at 525 nm, while the long axis had a surface plasmon resonance at 650 nm.

5 Characterization of Gold Nanorods

Gold nanorods are much smaller than the wavelength of visible light, thus we cannot use traditional microscopy to view them or characterize their alignment. However, there are several methods we can use to characterize the gold nanorods such as absorption profiles, dark field microscopy, two photon fluorescence, and electron microscopy.

5.0.3 Dark Field Microscopy

In dark field microscopy, we have a condenser which focuses the light. However the condenser also has an object which blocks the light which would travel straight to the objective lens. This allows us to only see scattered light. The liquid crystal which the gold nanorods are dispersed in scatters a much smaller amount of light than the gold nanorods, which means using the dark field lets us see only the gold nanorods within a sample. Furthermore, the

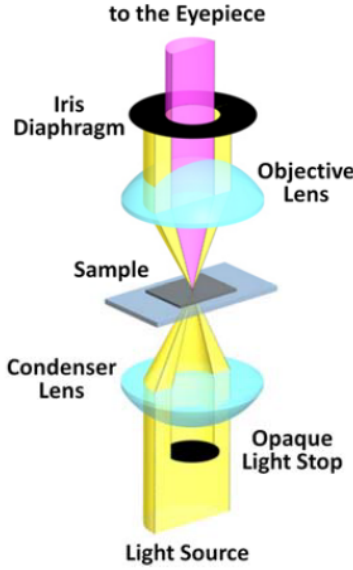


Figure 6: Schematic of a dark field microscope setup, notice that no transmitted light reaches the objective.[10]

scattered light from a point source covers a much greater area than the source does. Thus dark field microscopy allows us to view the positions of objects which are too small to see with conventional microscopy. If the dark field condenser is used with one polarizer, then we can also see the orientational order of the gold nanorods by viewing how the scattered color changes with the polarization.

5.0.4 Absorption Profiles

Gold nanorods have two surface plasmon resonances, one of which is driven by electron oscillations on the short axis of the rod, and another which is driven by electron oscillations on the long axis of the rod[16]. The SPR along the long axis responds to light polarized parallel to the long axis of the rod while the SPR along the short axis responds to light polarized perpendicular to the long axis of the rod. Thus to observe the degree of orientation of a collection of gold nanorods, we can view the absorption profiles at two perpendicular polarizations. If the gold nanorods are oriented isotropically, the absorption profile will not change with the polarization. If the gold nanorods are aligned then there will be a peak at 525 at one polarization and a peak at 650 at the other polarization (see fig. 7).

Furthermore, if the absorption profile differs from the regular absorption profile of gold nanorods, then we can conclude that something is wrong with the gold nanorods. This is an

easy way to check if there has been aggregation of the gold nanorods.

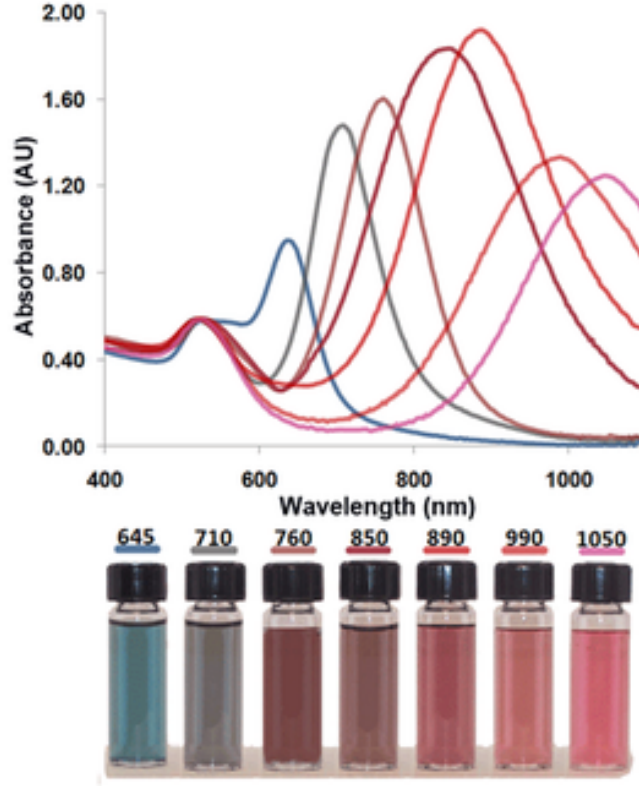


Figure 7: The absorption spectra for a two gold nanorods with different aspect ratios. The smaller peak at 525nm corresponds to the absorption from the short axis, while the larger peak corresponds to absorption from the long axis.[19]

5.0.5 Two Photon Fluorescence

Two photon fluorescence imaging is a powerful imaging technique which lets us image the dispersion and orientation of gold nanorods at small distances. The schematic of our setup is shown above. The basic principle is that we use a tunable wavelength laser beam to excite the gold nanorods with 850 nm light. The nanorods can absorb two of these photons, nearly simultaneously, to jump to a higher energy state. This energy state will quickly decay to a lower state without emitting radiation, and then will emit a photon and decay back to the ground state (see fig. 9). The emitted photon will have an energy which is approximately twice the energy of the original photon, which means that it will have a wavelength which is approximately half of the wavelength of the excitation light. After the light passes through the sample, we remove the excitation signal by running it through a low pass filter which

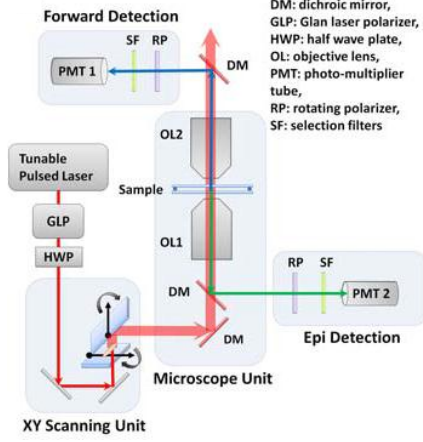


Figure 8: Schematic of our non-linear microscope setup. The setup is based on a pulsed laser, an XY scanning mirror, and an inverted microscope with multiple detection channels. [10]

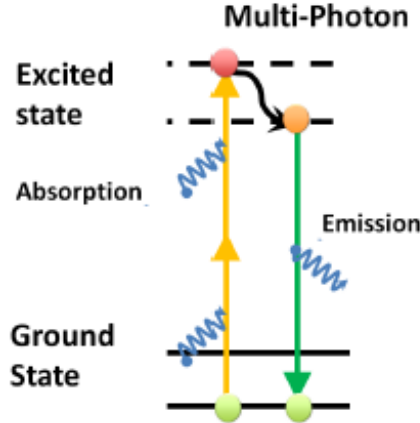


Figure 9: Schematic of multi photon process.[10]

removes every signal above 700 nm. The surface plasmon resonance of the long axis of gold nanorods is much greater than the surface plasmon resonance along the short axis of the gold nanorods[17] which means that the areas where the gold nanorods are aligned parallel to the polarization of the incoming light will have a much greater fluorescence signal than the areas where the gold nanorods are aligned perpendicular to the polarization of the incoming light. By adjusting the polarization angle of the incoming light it is possible to image both the dispersion and orientation of gold nanorods.

5.0.6 Electron Microscopy

The resolution of a conventional light microscope is limited by the visible wavelength of light[8]. Because of this it is theoretically impossible to resolve anything smaller than half of a micron. Electrons, however, have a much smaller wavelength (note the electron wavelength is given by the DeBroglie relation $\lambda = h/p$). Thus by using electrons rather than visible light, it is possible to view the gold nanorods themselves. We have used this imaging to verify that the gold nanorods did not aggregate within the cellulose nanocrystals, and we also used this to see if the gold nanorods were aligned parallel to the director.

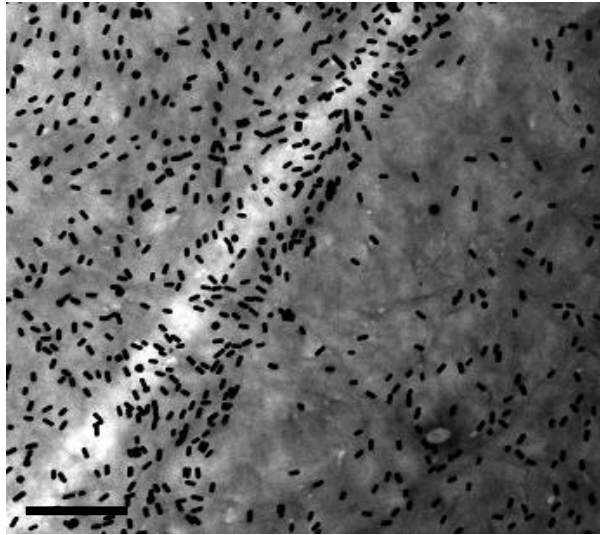


Figure 10: Transmission electron microscopy of a thin dried film of gold nanorods and cellulose nanocrystals. The magnification is 34000x, while the scale bar is 500 nm

6 Cellulose Nanocrystals

Cellulose is the most abundant and renewable biopolymer on earth; it has attracted scientific attention because it is cheap, nontoxic, and biodegradable.[18] Cellulose consists of several glucose units which are linked together.[18] These cellulose molecules can also bind together to form a crystal, where instead of atoms on a lattice, there are cellulose molecules in a lattice arrangement[3]. Within a natural source of cellulose, such as wood, or bacterial cellulose, the cellulose will be in two regions. One region consist of dense crystalline cellulose molecules,

which are tightly bound together, the other is less dense and consists of cellulose molecules which are amorphously bound together.[18] The crystalline regions have a specific structure to them and are normally 10nm thick by 300 nm long[18]. These dense crystalline regions are known as cellulose nanocrystals. Due to their long thin shape, they are sometimes referred to as whiskers in the literature.

When cellulose is subjected to sulfuric acid hydrolysis, the hydronium ions can penetrate and hydrolyze the amorphous regimes of a cellulose source. However, the cellulose nanocrystals are too dense for the hydronium ions to penetrate, which means that acid hydrolysis can be used to generate relatively defect free cellulose nanocrystals.[3]

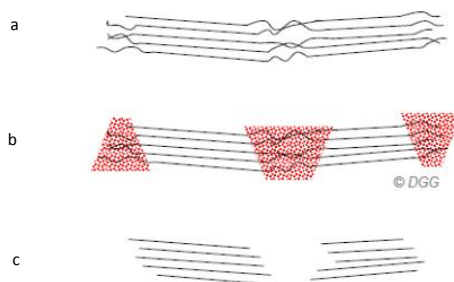


Figure 11: Illustration of how CNC's are synthesized. Initially the cellulose consists of ordered and disordered regions (a). Upon acid hydrolysis, the hydronium ions (represented by red dots) will dissolve the amorphous regions (b), leading to defect free cellulose nanocrystals (c). (image taken from [25])

6.1 LC phases of cellulose nanocrystals

In 1949, Onsager showed that a collection of rods which are dispersed in a solvent will form a nematic phase once the concentration is increased beyond a critical volume concentration.[1] This critical volume concentration, labeled ϕ , depends on the aspect ratio of the rod, $\phi \propto \frac{D}{l}$ [1], where D is the diameter of the rod and l is the length of the rod. Once the volume concentration is greater than ϕ , the translational entropy of the rods will be maximized by parallel alignment, which leads to a nematic phase. Onsager's theory was expanded upon by Stroobants, Lekkerkerker, and Odijk, who generalized it to the case of charged rods. In the case of charged rods, they found that a solution will have two phases, cholesteric and isotropic.

These two phases will coexist in equilibrium. The volume fraction occupied by each phase depends on the concentration, going from being completely isotropic at low concentrations, to being completely cholesteric at high concentrations.[14]

During the acid hydrolysis negatively charged sulfate groups will bind to the end of the cellulose nanorods. The negatively charged sulfate groups will cause the cellulose nanocrystals to repel from each other[18], which prevents aggregations, but also causes them to be described by SLO theory[21]. Cellulose nanocrystals will naturally form a cholesteric phase, which coexists with the isotropic phase. Typically we have observed that the cholesteric phase separation does not begin normally until a weight percentage well over 3 percent.

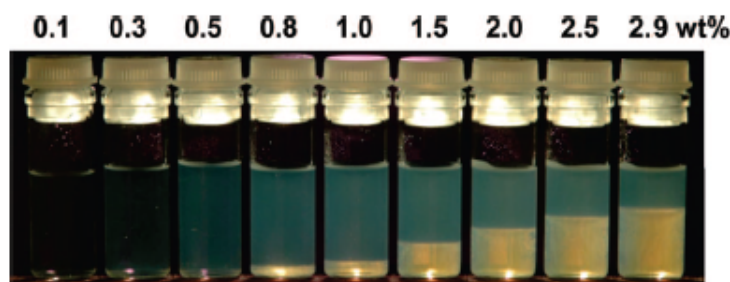


Figure 12: Photograph of bacterial CNC dispersed in water at different concentrations. As the concentration increases the volume fraction of the cholesteric phase (bottom) increases[20]

7 Self Assembly of Gold Nanorods in Cellulose Based Liquid Crystals.

One of the goals of our lab has been to demonstrate that it is possible to align large quantities of gold nanorods using the self assembly of liquid crystals. So far, however, in many liquid crystal systems the gold nanorods will aggregate which destroys the surface plasmon resonance that we are hoping to achieve. I have demonstrated in my research that we can use a solution of cellulose nanocrystals dispersed in water to align large quantities of gold nanorods.

In the case of small molecule liquid crystals like E7 or 5CB, the gold nanorods cause the director of the liquid crystal to twist around the gold nanorod [11]. These twists of the director cost energy. However the energy of these defects is minimized when the gold

nanorod is aligned parallel to the director, which causes the gold nanorods to align parallel to the director.[11]

Since gold nanorods are much smaller than cellulose liquid crystals, it is unlikely that the gold nanorods would create energetically costly defects within cellulose based liquid crystals. However, to predict the alignment of gold nanorods we can again turn to Onsager's theory. In this case, the translation entropy of both the cellulose and the gold nanorods will be maximized when the gold nanorods are aligned parallel to the cellulose nanocrystals. However, this alignment will only happen after a certain concentration of cellulose is reached.

8 Methods

8.1 Preparation of Cellulose Nanocrystals

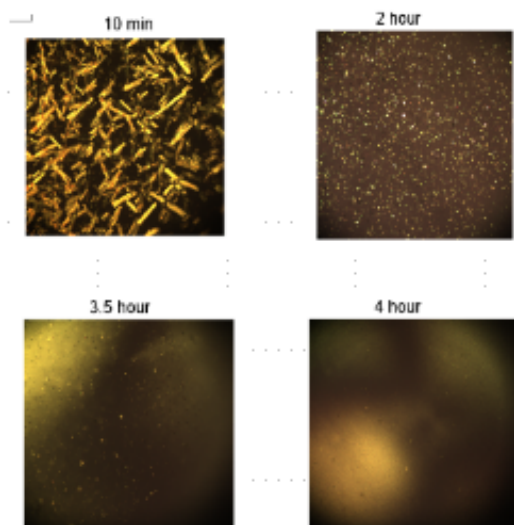


Figure 13: Cross polarized images at 10x showing the degradation of cellulose in 65% sulfuric acid solution.

To create the cellulose nanocrystals I used a similar method to the group ran by Shopowitz [24]. I began by combining 5-10 grams of bleached cotton with 75-150 mL of 65 wt% sulfuric acid (approximate 15g acid solution per gram of cotton). The solution was heated and maintained at 45 degrees celcius for 2-8 hours with vigorous stirring, while being placed in the sonifier for 5-10 minutes every one to two hours. We found that the cellulose could not completely degrade without the sonification. Every hour, a small amount of the solution

was extracted and observed under cross polarized microscopy to check the degradation of the cellulose. A representative sample of these images is shown above. After the cellulose had completely dissolved we quenched the reaction by adding a large amount of DI water. After this we washed the solution several times via centrifugation, which increased the PH and removed the soluble byproducts of cellulose. At this step the solution would still have a pH of 1. To increase the pH further we placed the solution inside of a dialysis membrane and let it dialyze against DI water. The DI water was occasionally replaced, and the dialysis continued until the DI water maintained a constant pH, which was normally 2-3 days. After this, the cellulose nanorods were filtered with a three micron filter. At this stage the concentration of cellulose was normally 2-3 percent in weight.

8.2 Preparation of Gold Nanorods

We used gold nanorods which were supplied by Nanopartz. The nanorods were first dispersed in water. To prevent aggregation we capped the nanorods with Methoxy polyethelyne glycol (MPEG), which is a ligand which prevents the gold nanorods from coming close enough to each other to aggregate. To achieve this we combined 300 μL of Gold nanorods with 250 μL of a 10 % by wt. of MPEG in water. This mixture was then added to 10 mL of DI water and then let sit for 12 hours to allow the MPEG to bind to the gold nanorods. After this, we centrifuged the rods and decanted the supernatant, and then added another 250 μL of MPEG solution and 10 mL of water. We again let this solution sit and then centrifuged it to obtain MPEG capped gold nanorods. The purpose of adding MPEG twice was to ensure that the gold nanorods were completely capped with the MPEG.

8.3 Verifying the Dispersion of Gold Nanorods

To verify that the gold nanorods had dispersed within the solution and had not aggregated I used dark field microscopy and scanning tunneling electron microscopy. The dark field images showed there was little to no aggregation at cellulose concentrations of 3% wt. To verify this I also used transmission electron microscopy to image the gold nanorods and cellulose.

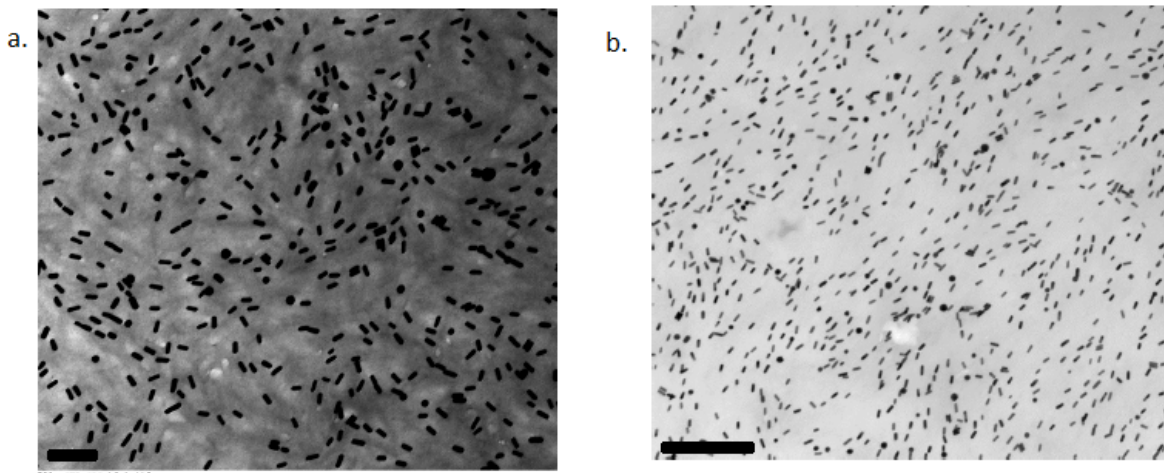


Figure 14: SEM images of a thin film of GNR's and CNC's. This image shows that the gold nanorods did not aggregate. a. The magnification is 46000x, and the scale bar is 200nm. b. The magnification is 34000x, and the scale bar is 500 nm.

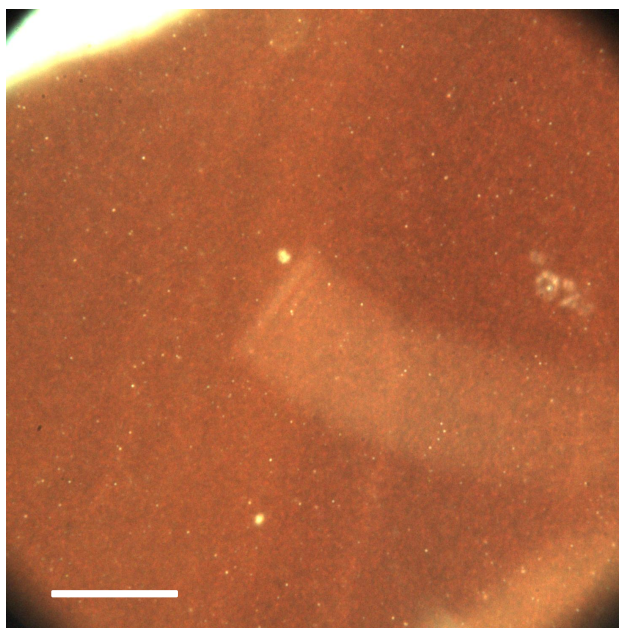


Figure 15: Dark field image of gold nanorods dispersed in cellulose nanocrystals. The lack of any solid structures indicates that there was little to no aggregation. The scale bar is 30 microns.

9 Methods of Aligning Cellulose Nanocrystals Using Nematic Mesophase Formation

Cellulose has a chiral structure which causes it to form a chiral nematic phase[18]. However there are several methods which can be used to create thin films of aligned cellulose nanorods.

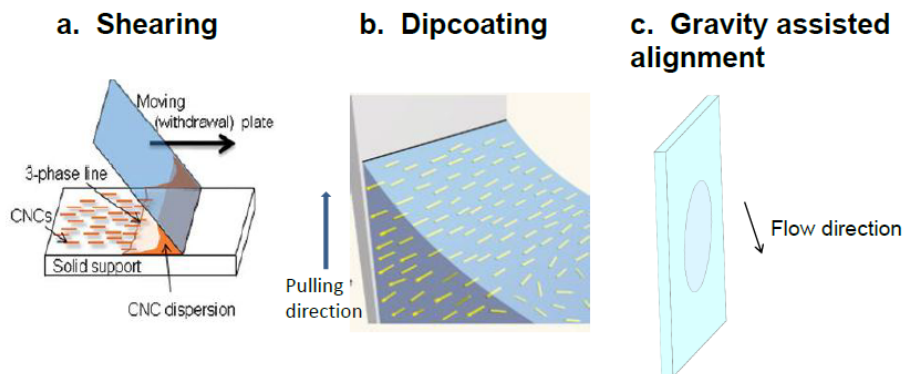


Figure 16: Schematic of the three different methods we used to align cellulose nanocrystals. (a) is taken from [22], (b) is taken from [23]

Some examples are shearing, shearing while applying an electric field, and using a large (7 Tesla) magnetic field[13]. These methods use the combination of several forces to align the liquid crystal. When cellulose flows, the rods can align parallel to the direction of flow, or they can tumble in which case the director has no preferred orientation. This behavior has been found to depend on the ratio of two Leslie viscosities[13]. Also capillary forces can cause the liquid air interface to be curved. In that case the cellulose nanorods will align parallel to the interface along the direction of least curvature in order to avoid director distortions..

In our research we focused mainly on using the convective forces (flow) and capillary forces (the forces in a meniscus) to align gold nanorods. The methods that we used included shearing (convective and capillary forces), dipcoating (mainly capillary forces), and gravity assisted alignment (mainly convective forces).

9.1 Shearing-Assisted Alignment

Within a shearing assembly, the liquid crystal is held by capillary forces in the meniscus formed by a moving glass plate and a glass substrate. The moving glass plate is slid across the assembly at a slow speed. The liquid crystal will deposit itself in ultrathin layers on the substrate, which leads to a 3 phase contact line on the edge of the meniscus, where there is solid CNC solution, evaporated water vapor, and solidified CNC films.

When cellulose is subjected to convective shearing, a variety of complex forces will act on the cellulose nanorods. There are electrostatic repulsions between the cellulose nanocrystals and the gold substrate which tend to randomly align the nanocrystals. There are also shear

and capillary forces which act parallel and perpendicular, respectively, to the 3 phase contact line [13]. By controlling the withdrawal speed it is possible to adjust the ratios of the various forces so that the nanorods will align parallel to the withdrawal direction [13]. By repeating this process several times, it is possible to create a thin uniformly aligned film of cellulose nanocrystals and gold nanorods.

9.1.1 Methods

We began by combining a solution of cellulose nanocrystals at a concentration of 5% by weight with concentrated gold nanorods dispersed in water. We found that a higher concentration of cellulose nanocrystals allowed us to create a denser ordered layer. To ensure that the nanorods were well dispersed in the liquid crystal we sonicated the solution for an average time of 30 minutes.

To shear the solution, we used a glass substrate and either a razor blade or a glass slide to create the meniscus, which was held slightly above the glass slide. We then pipetted a small amount (30 microliters or less) of cellulose and gold nanorod solution between the substrate and the glass slide. The slide was then moved back and forth at a slow speed. Each time the slide was moved back and forth, a thin coating of cellulose and gold nanorods was deposited. After all of the liquid had evaporated, we repeated the procedure with another small amount of the solution. This normally continued until approximately 50-150 microliters of solution had been deposited.

9.1.2 Results

Using this method we could not achieve a highly ordered thin film of gold nanorods and cellulose nanocrystals. This was most likely due to a large variance in the speed of shearing. The speed of shearing has a large impact on the order of a cellulose film which is maximized at a shearing rate of 8.4 cm/hr[13]. This method had the advantage of being able to produce thick films in a relatively quick amount of time; however, films produced by the other methods we used tended to be more ordered.

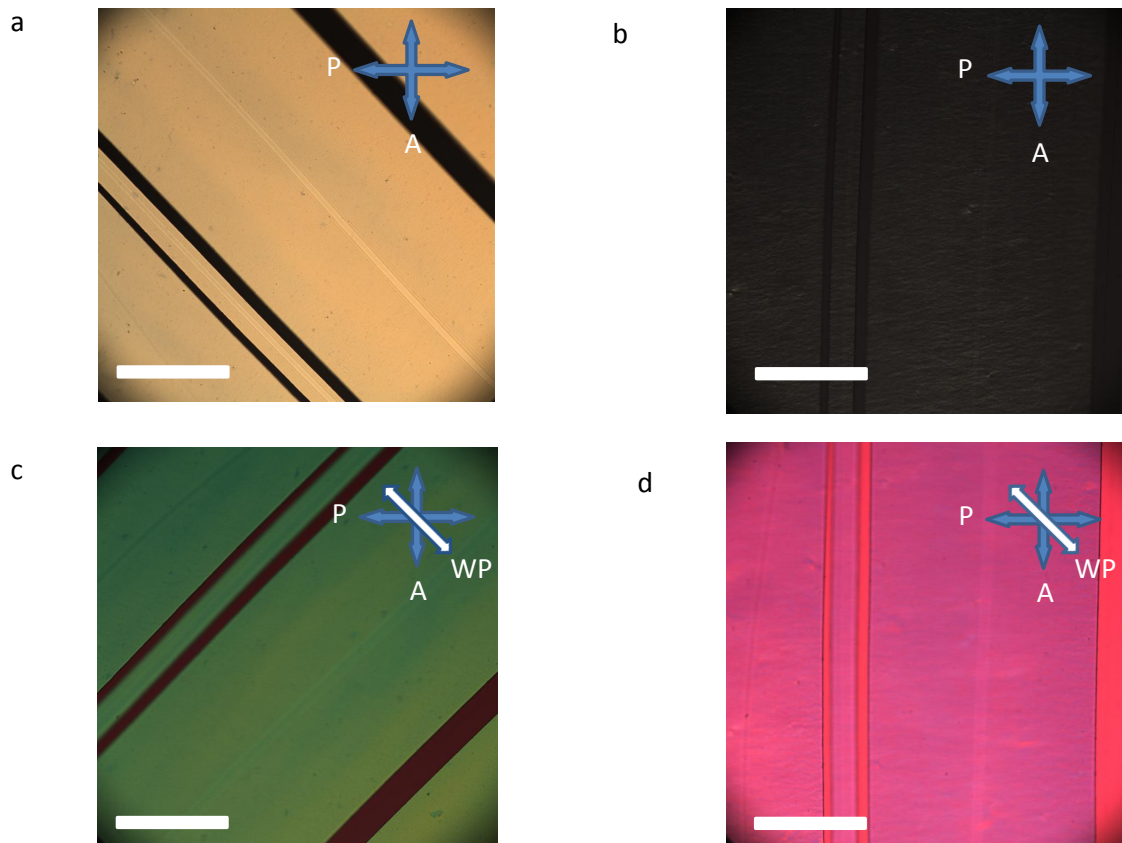


Figure 17: a,b. Cross polarized microscopy images of thin films of cellulose nanocrystals obtained by shearing oriented with the director at 45 (a) and 0 degrees from the cross polarizers. c,d. Cross polarized images with a quarter waveplate of thin films obtained by shearing. The scale bar for all of these images is 200 microns. The direction of shearing was parallel to the dark stripes.

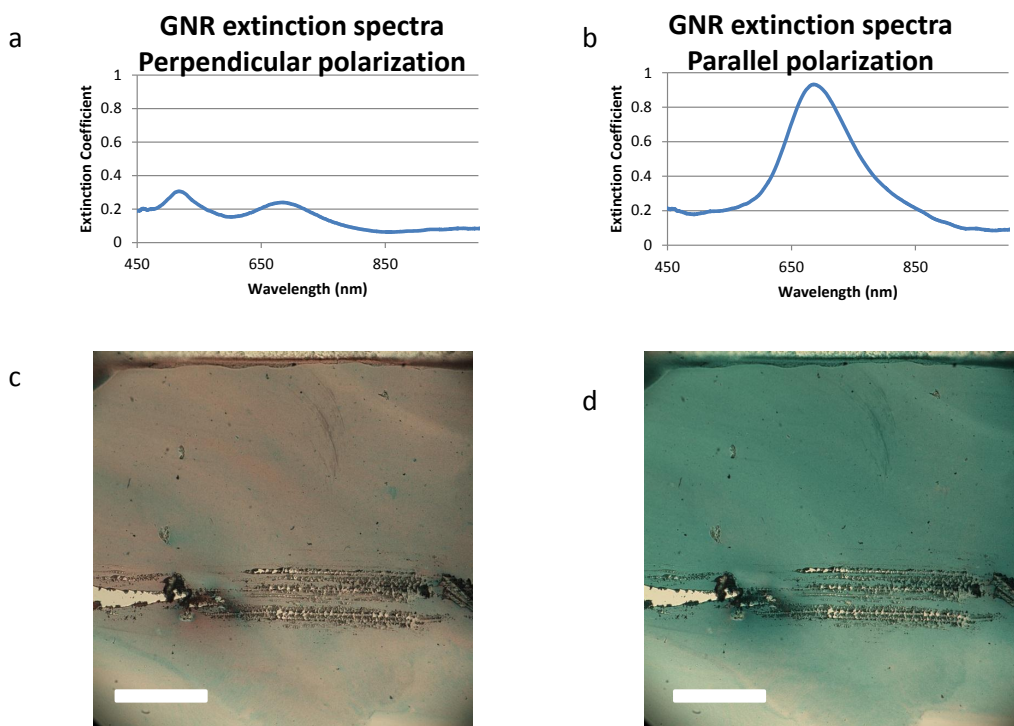


Figure 18: a,b. Extinction coefficients of the thin films of cellulose nanocrystals and gold nanorods with light polarized 0 (a) and 90 (b) degrees with respect to the director. c, d. Images of a thin film of gold nanorods and cellulose nanocrystals obtained by shearing with an analyzer aligned perpendicular (c) and parallel (d) to the director. The scale bar is 70 microns.

9.2 Dipcoating-Assisted Alignment

Dipcoating consists of slowly pulling a slide out of a solution of cellulose nanocrystals and gold nanorods. Between the slide and the solution a meniscus will form. In order to avoid director bend and splay distortions, the molecules will align parallel to the three phase contact line (see fig 16). As the film is pulled the contact line will move upwards at a slow rate. At the substrate, air, liquid interface, CNC and GNR will be deposited onto the substrate, producing a thin aligned film. In contrast to the other methods that I had used, in this method the withdrawal is very slow, which means that convective forces are less important in the alignment of the cellulose nanocrystals than in other methods. Since the capillary and convective forces act perpendicular to each other, by minimizing one of the forces we were able to achieve highly aligned films.

9.2.1 Methods

We used a stock cellulose solution of 3 % cellulose nanocrystals by wt. and added concentrated gold nanorods to the mixture. The mixture was then shaken, and briefly sonicated to promote dispersion of the gold nanorods. We used a stepper motor, which was driven by a computer to achieve a constant withdrawel speed. To increase the thickness of the films we used glass substrates which were first treated with parahna solution. Parahna solution will cause a glass substrate to become hydrophilic, which we found to increase the thickness of the films. The substrates were then attached to a stepper motor which would pull the slides at a slow constant rate. The substrates were then lowered into a cuvette of cellulose and gold nanorod solution, and raised at a constant rate of approximately 1 cm/hr. In our experiments, we found that the alignment did not greatly depend on the speed. This procedure was normally repeated more than once to create a thicker layer of cellulose.

9.2.2 Results

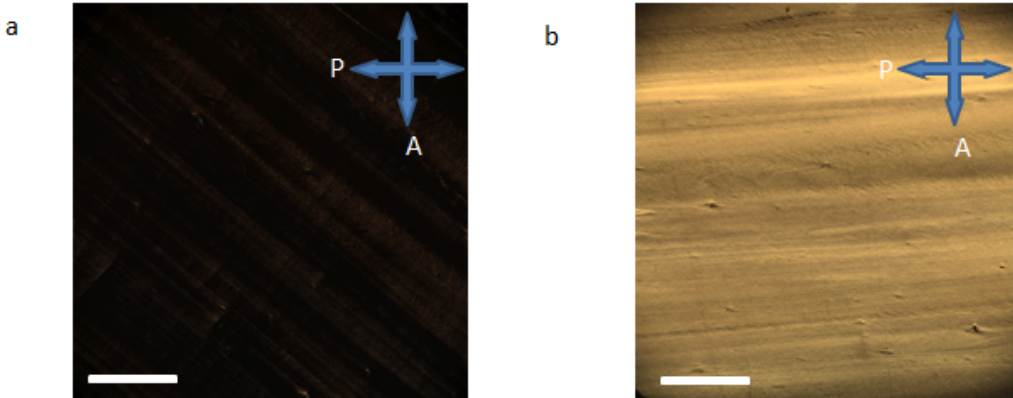


Figure 19: Cross polarized images of cellulose films obtained by dipcoating at angles of 45 (a) and 0 (b) degrees with respect to the cross polarizers. The scale bar is .3 mm. The withdrawel direction was perpendicular to the stripes.

This method produced highly aligned films of gold nanorods. The areas of alignment were very large covering over 1 square cm. Observing the thin films of cellulose nanorods through cross polarized microscopy revealed that the films were very highly ordered with very little defects. However, this method had two downsides which prevented it from being used to create thin films.

The first was the substantial use of materials. While the other methods only needed less than 100 microliters of gold nanorod and cellulose nanocrystal solution, dipcoating required at least 4 mL. The second was the time, dipcoating one layer would take several hours. Since the layers were incredibly thin, dipcoating enough to see the gold nanorods would take a week just for one slide. In that time, the cellulose solution would also evaporate, leaving a thin solid film on top of the cuvette, which was not highly ordered. Thus it would be difficult to repeat this procedure long enough to create a reasonably thick film. We found that these limiting factors made it impossible to create a film that is dense enough to have the desired absorption properties.

9.2.3 Evaporative Dipcoating: Method and Results

We also used evaporative dipcoating, where instead of mechanically pulling the slide out, we placed a solution of cellulose nanocrystals and gold nanorods in a cuvette along with a glass substrate that had been cleaned with parahna solution. Again, the meniscus aligns the cellulose as it is evaporating. The cellulose tended to form highly ordered layers. However, like the dipcoating method, this method took a long time, and required a substantial use of materials. Thus we did not pursue this method in our research.

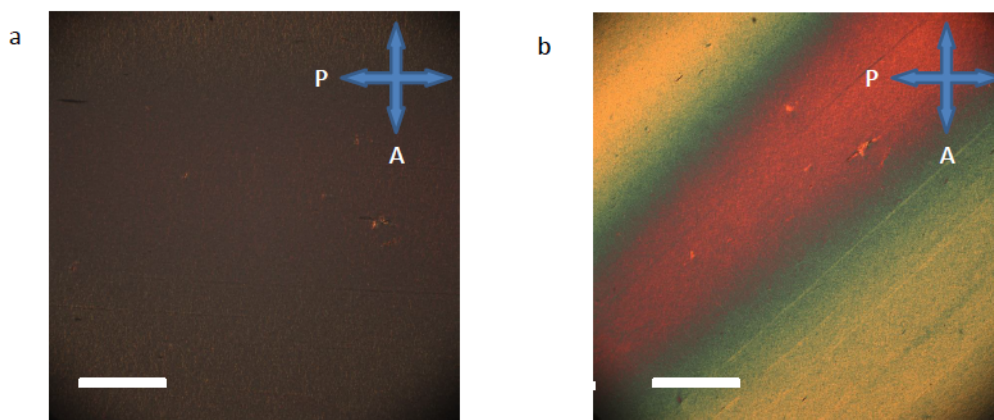


Figure 20: Cross polarized image of the cellulose films obtained by evaporative dipcoating with the director at 45 (a) and 0 (b) degrees with respect to the cross polarizers. The scale bar is .3 mm. The evaporation direction was perpendicular to the stripes.

9.3 Gravity-Assisted Alignment

In this method we sought to control the convective forces as a primary method to align the cellulose nanorods. To control the flow of liquid crystal we used gravity. In our setup we placed a glass substrate at an angle of 70-80 degrees. A concentrated solution of gold nanorods and cellulose nanocrystals dispersed in water was placed at the top of the slide, and allowed to flow down under the action of gravity. After the solution had reached the bottom it was recovered with a pipet and again placed at the top of the slide. We continued this process until the entire solution had dried.

Upon analysis we found that on the two outer regions of cellulose nanocrystal flow, we had thick well aligned films of gold nanorods and cellulose nanocrystals. We found that the films were thickest along the edge of the flow area, and in these areas the films also had the highest amount of alignment. Within these areas the absorption spectra of these gold nanorods had two well defined surface plasmon resonance peaks, which appeared when the light was polarized parallel and perpendicular to the director of the cellulose nanocrystals.

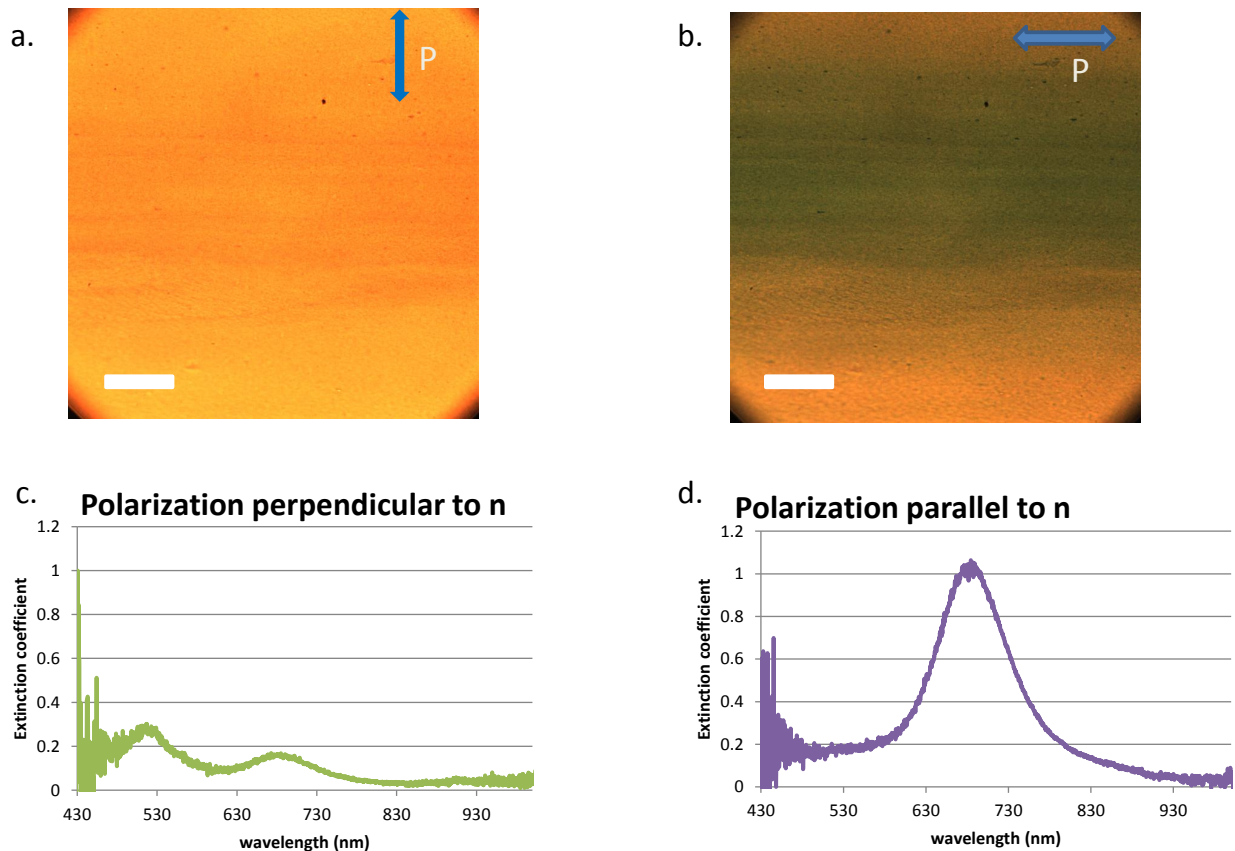


Figure 21: a,b. Bright field image of a thin film of gold nanorods and cellulose nanocrystals with one polarizer oriented perpendicular (a) and parallel (b) to the director. The scale bar is 50 microns. c,d. Extinction spectra of the films with the polarization perpendicular (c) and parallel (d) to the director.

10 Cholesteric Alignment of Gold Nanorods Within Cellulose Based Liquid Crystals

The cholesteric phase of cellulose only occurs at high concentrations of cellulose. During evaporation of the cellulose nanorods in a solvent, the cellulose will remain in an isotropic state until a cholesteric transition point is hit. At that point the cellulose nanorods will begin to form droplets of cholesteric liquid crystal, where within the droplets the liquid crystal is cholesteric, and outside the droplets, the liquid crystal is isotropic.[26] Over time these droplets will merge into a larger region of cholesteric phase, which will coexist in equilibrium

with the isotropic phase.[26] Furthermore, as these droplets merge, the pitch will shrink, going from 20 microns for the first tactoids, to 5-6 microns for the fully formed cholesteric region.[26]

In this phase, aggregation of the gold nanorods was much more of an issue than it was in nematic alignment. Within the cholesteric region, the gold nanorods will be aligned along the liquid crystal in order to maximize translational entropy, which means they will not possess any rotational degrees of freedom. Furthermore, the cellulose is denser within the cholesteric regions which means there is a larger excluded volume in the cholesteric region. However in the isotropic state the gold nanorods will possess three rotational degrees of freedom and a smaller excluded volume. Thus from entropy considerations alone, the gold nanorods should tend to accumulate within the isotropic regions.

10.1 Methods

We found that evaporating a solution of cellulose nanocrystals and gold nanorods, we could not achieve cholesteric alignment of the gold nanorods. After imaging these solutions we found that the gold nanorods had aggregated outside of the cholesteric regions. To limit the dispersion of gold nanorods from the cholesteric regions, we induced a fast phase change.

To accomplish this, we started with a cellulose nanocrystal solution that was biphasic. We then added gold nanorods to an isotropic solution, and then shook them using the vortex shaker. By doing this we dispersed the gold nanorods within the isotropic phase. We then centrifuged the mixture. This caused the cellulose nanorods to form a cholesteric phase at the bottom of the vial and the gold nanorods to settle at the bottom of the vial. We then drained the supernatant isotropic phase, and then sonicated the mixture. The increase in CNC concentration induced a phase change which occurred within minutes. Because of this, the gold nanorods remained inside of the cholesteric phase long enough for us to image their alignment. To image the gold nanorods within this phase we used two photon fluorescence imaging. We took the two photon images at both 0 and 90 degree polarizations so that we could image not only the dispersion of gold nanorods, but also their orientation.

10.2 Results

By inducing a fast phase transition we were able to disperse gold nanorods within the cholesteric regions. The fluorescence signal was much higher outside of the cholesteric regions, which indicates that the cellulose nanocrystals tended to accumulate outside of the cholesteric regions. After imaging the same sample several days later, the fluorescence signal from the cholesteric regions had completely vanished. During the imaging we found that the gold nanorods were aligned parallel to the director of the cellulose nanocrystals within the cholesteric regions.

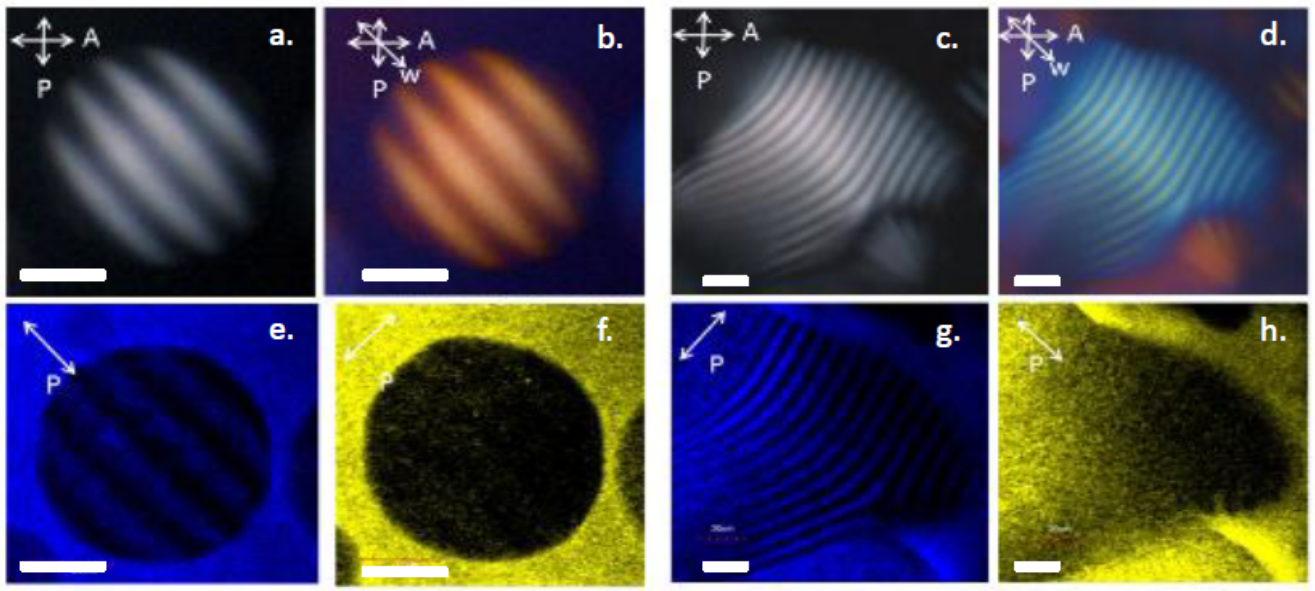


Figure 22: Two Photon Fluorescence imaging of Gold Nanorods within cholesteric regions of a solution of cellulose nanocrystals. a,b. Cross polarized microscopy image of a solution of cellulose nanocrystals in water with (b) and without (a) a waveplate. e,f. Two photon luminescence imaging of gold nanorods in a solution of cellulose nanorods in water. The direction of excitation light is polarized parallel (e) and perpendicular (f) to the director of the cellulose nanocrystals. c,d. Cross polarized microscopy of a solution of cellulose in water without (c) and with (d) a waveplate. g,h. Two photon fluorescence imaging of gold nanorods in a solution of liquid crystals with the polarization of excitation light at an angle of 45 (g), and 135 (h) degrees from the xy plane. The scale bar in all images is 20 microns.

11 Conclusions and Future Directions of Research

My research has shown that it is possible to align gold nanorods at high concentrations within thin films of ordered cellulose nanocrystals. Within the highly aligned regions there

is a large polarization dependent surface plasmon resonance. This could be used to fabricate plasmonic polarizers, which would have a wavelength dependent polarization. However the areas of alignment are quite small compared to what we want to achieve, thus a future direction of research would be exploring how to achieve larger areas of dense concentrations of gold nanorods. We have not yet used electric and magnetic fields, which could, in principle lead to greater alignment, and this is something we plan to do in the near future. I will also work on theoretical modeling of the experimental findings.

12 Acknowledgments

I would like to thank Ivan Smalyukh for the opportunities and guidance he has given me. I would also like to thank Qingkun Liu for teaching me the fundamentals of how to conduct research in a laboratory. I'd also like to thank everyone in the lab who has helped me at one point or another, especially Julian Evans and Bohdan Senyuk.

References

- [1] P.G. DeGennes and J. Prost, *The Physics of Liquid Crystals*, Clarendon Press, Oxford.
- [2] A. Anu, and N. Engheta, "Achieving Transparency with Plasmonic and Metamaterial Coverings", Phys. Rev. E, 72, 016623, (2005) <http://arxiv.org/abs/cond-mat/0502336>
- [3] Y. Habibi, et all. Cellulose Nanocrystals: Chemistry, Self-Assembly, and Applications, Chem Rev. 110, 3479-3500, (2010)
- [4] K. J. Stebe et. all. "Oriented Assembly of Metamaterials," M. Science 325, 159 (2009)
- [5] I. W. Hamley, *Introduction to Soft Matter*, Wiley, New York, p223
- [6] W. J. Orts et. all "Enhanced Ordering of Liquid Crystalline Suspensions of Cellulose Microfibrils: A Small Angle Neutron Study," Macromolecules, 31,5717-5725 (1998)
- [7] Liquid Crystals, Cambridge University, 2012, <http://www.doitpoms.ac.uk/tlplib/anisotropy/liquidcrystals>.
- [8] J. Pendry and D. Smith, "The Quest for the Superlens," Scientific American 295, 60, (2006)
- [9] Bayman, Hamermesh, *A Review of Undergraduate Physics*, Wiley, New York, 1986
- [10] T. Lee et. all. "Optical Microscopy of Soft Matter Systems," <http://arxiv.org/ftp/arxiv/papers/1108/1108.3287.pdf>
- [11] I.I. Smalyukh et. all. "Elasticity-Mediated Nematic-Like Bacterial Organization in Model Extracellular DNA Matrix," Phys. Rev. E. 78, 030701, (2008)
- [12] T. Pullawan et. all "Influence of Magnetic Field Alignment of Cellulose Whiskers on the Mechanics of All-Cellulose Nanocomposites," Biomacromolecules, 13, p2528-2536, (2012).
- [13] I. Hoeger et. all. "Ultrathin Film Coatings of Aligned Cellulose Nanocrystals From a Convective Shear Assembly System and Their Surface Mechanical Properties," Soft Matter, 7, 1957 (2011)
- [14] A. Stroobants et all. "Effect of Electrostatic Interaction on the Liquid Crystal Phase Transition in Solutions of Rodlike Polyelectrolytes", Macromolecules, 19, 2232-2238, (1986)

- [15] General: Plasmonics, 2012, nanoComposix, 2012,
<http://nanocomposix.com/kb/general/plasmonics>
- [16] S. Maier, *Plasmonics: Fundamentals and Applications*, p72, Springer, New York, 2007
- [17] H. Wang et al. "In vitro and in vivo two photon luminescence imaging of single gold nanorods", PNAS, v102, p15752-15756, (2005)
- [18] W. Hamad, "On the Development and Applications of Cellulosic Nanofibriller and Nanocrystalline Materials", Canadian J of Chem Eng. v84, 513-519, (2006)
- [19] Tomowave Labs, 2012, <http://www.tomowave.com/nanotechnology.html>
- [20] A. Harai et. al. "Phase Separation Behavior in Aqueous Suspensions of Bacterial Cellulose Nanocrystals Prepared by Sulfuric Acid Treatment," Langmuir, 25, 497-502 (2009)
- [21] X. M. Dong et. al. "Effect of Ionic Strength on the Isotropic-Chiral Nematic Phase Transition of Suspensions of Cellulose Crystallites," Langmuir, 12, 2076-2082 (1996)
- [22] I. Hoeger et. al Soft Matter, 7, 1957-1967, (2011)
- [23] I. I. Smalyukh, "Deft Tricks With Liquid Crystals," Nature, 478, 330-331 (2011)
- [24] K. Shopowitz et. al. "Free Standing Mesoporous Silica Films with Tunable Chiral Nematic Structures," Nature, 468, 422-425 (2010)
- [25] D. Grey, "Liquid Crystalline and Gelling properties of Cellulose Nanocrystal suspensions," International LC elastomer conference, Lisbon Sept 11, (2011)
- [26] J. F. Revol et al. "Helicoidal Self-Ordering of Cellulose Microfibrils in Aqueous Suspension," Int. J. Biol. Macromol., 14, 170-172 (1992)