The Assembly and Alignment of Nanoparticles in Liquid Crystals

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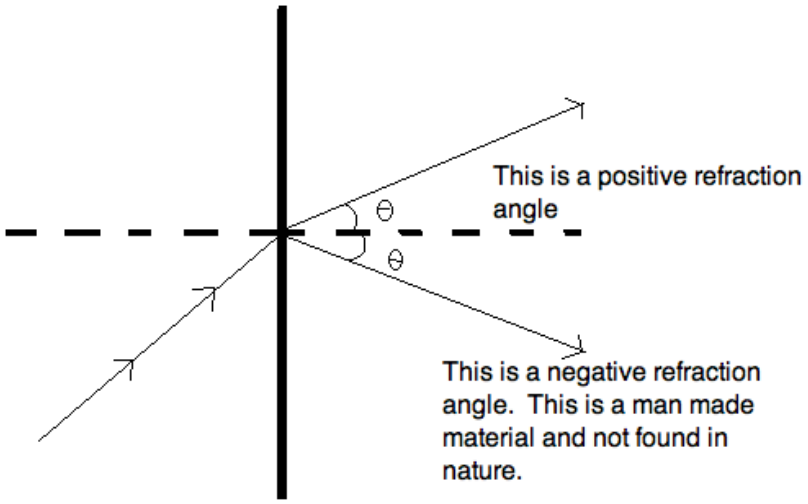
I. Introduction

Our goal was to align nanoparticles in liquid crystals. The first step to achieve this goal was to synthesize nanoparticles. "Nanoparticles" is a very broad term, referring to particles with dimensions in nanometers. When nanoparticles are mentioned in this paper, it means nanospheres or nanorods unless specified otherwise. However, many shapes of nanoparticles exist, such as decahedra, squares, triangles and even nanodogbones, which will be briefly talked about later. Additionally, nanoparticles are made of many different materials. This paper discusses gold and silver nanoparticles, but semi-conducting materials can also form nanoparticles. Nanorods are of great interest because when assembled in an ordered structure they form a metamaterial. Some metamaterials are materials that have a negative refractive index:



These metamaterials could in the future be used to make a "perfect lens" or an "invisibility cloak." While the construction of either would have a great impact, both of these names are a little deceiving; the perfect lens would not be perfect because there would still be a limit to the focus, but it would significantly increase the resolution of light, and the invisibility cloak would make objects invisible but unlike Harry Potter's invisibility cloak, anything inside the cloak would be blind to the world outside.

Metamaterials have been made and successfully demonstrated in the microwave wavelength. To make a metamaterial, the design must be smaller than the wavelength of the wave you are manipulating. For visible light, much smaller designs are required than for microwaves. These designs are on the nano scale. The most modern nanofabrication technologies use lasers or electrons to fabricate designs. However, metamaterial designs for visible light need designs beyond the current capabilities of nanofabrication; the designs required are too small and current technology is not an efficient way to make them.

Liquid crystals self assemble into nanostructures of many different shapes and sizes all dependent on the materials and concentrations used. Combining nanoparticles, which are smaller than the wavelengths of visible light, and liquid crystals, which self-assemble into ordered structures on the nano scale, one can imagine forming a structure of nanoparticles. An ordered assembly of nanorods has been suggested as a design for a metamaterial and this design resembles nanoparticles in a nematic liquid crystal. A nematic liquid crystal is a phase when the micelles have long-range orientation but the micelles do not have positional order. If liquid crystals can be used to self-assemble nanoparticles into metameterials, it would greatly advance the field and its possibilities, making production and experimentation cheaper and less time-consuming as well as making mass production feasible.

II. Lyotropic Liquid Crystals

Liquid crystals are a state of matter between an isotropic fluid and a solid. There is long-range orientation but no positional order. In the picture below of the liquid crystal the long-range orientation would be in the north-south direction.

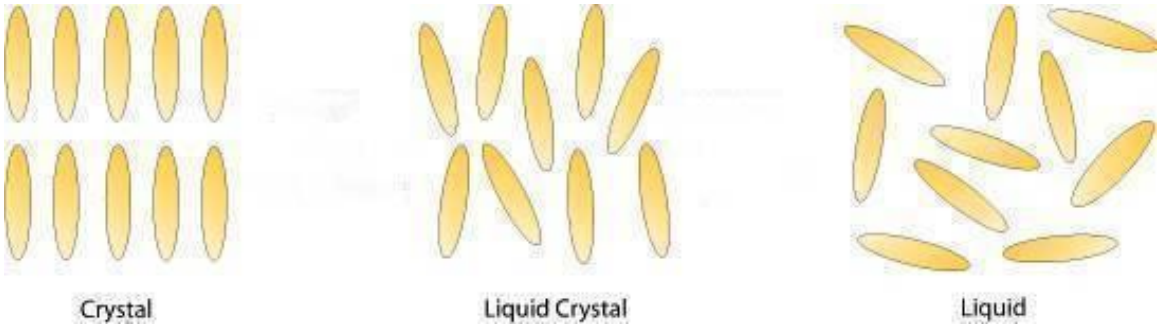


Figure 1: Three different states of matter, crystal, liquid crystal and liquid.

There are many types of liquid crystals; we work with lyotropic liquid crystals. Lyotropic liquid crystals are made with a molecule that has a polar head and a hydrophobic tail. When this molecule is introduced to water, the hydrophobic tail does not want to mix with the water while the polar head does. This causes the molecules to form micelles. The polar heads stick out towards the surrounding water while the tails hide in the center of the space the polar heads have created. Micelles come in different sizes and shapes but are all on the nanoscale. Their shape and size can be controlled by the concentrations of the materials used to make the liquid crystal. These different shapes and sizes are characterized by the phase of the liquid crystal.

There are many different phases of liquid crystal, some of which will be discussed in this paper. A nematic phase liquid crystal has rod-like micelles and looks like the liquid crystal cartoon above where the rod shapes represent the micelles. A hexagonal phase liquid crystal has rod-like micelles, but they are more concentrated. The rods stack together in a hexagonal shape giving the phase its name. There is a cubic phase of liquid crystal; this resembles the cubic structure of a solid crystal of atoms except that instead of atoms in the cubic lattice, spherical micelles are in the cubic lattice. The last phase of

liquid crystal that we regularly work with is the cholesteric liquid crystal. This liquid crystal is also made up of rod-like micelles. A chiral molecule added to the liquid crystal causes the rod like micelles to stack one upon the other at a slight angle.

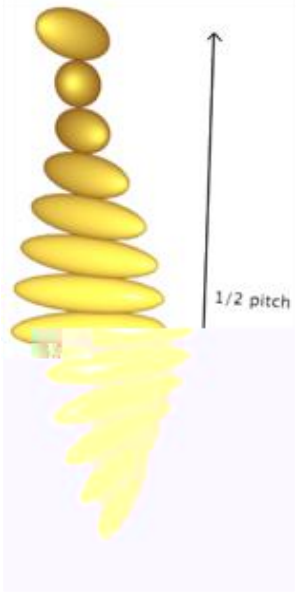


Figure 2: The pitch in a cholesteric liquid crystal.

The rods in this picture represent the rod-like micelles formed and then stacked slightly skewed on top of each other. When the micelles have made a complete twist of 360 degrees they have made a complete pitch. In the figure to the left, the molecules have only twisted 180 degrees and so have completed only half a pitch.

Figure 3: XZ scan of a cholesteric liquid crystal.

In the figure above, a cholesteric liquid crystal has been doped with a fluorescent dye and imaged in the confocal microscope. The dye is bright or dark depending on its orientation to the camera. The dye has aligned itself with the liquid crystal molecules and so the layers represent a half pitch within the liquid crystal. The layers are only half a pitch because the dye looks the same at 180 and 360 degrees of rotation.

Some metamaterial designs that have been suggested resemble the phases of liquid crystals. Metamaterials need metal and this is why we are attempting to put nanorods into liquid crystals and use the self-assembling nature of the liquid crystals to assemble the nanorods for us.

III. The Synthesis of Gold Nanoparticles

All solutions were made with de-ionized water prepared within a few days of preparation.

Seed Solution: To make seed solution, 5 mL of a .20 M solution of Hexadecyltrimethylammoniumbromide (CTAB) was prepared and mixed with 5 mL of a .00050 M $HAuCl_4$ solution. As the solution was stirring, .60 mL of cold $NaBH_4$ was added. The $NaBH_4$ was kept as close to frozen as possible. The addition of the $NaBH_4$ turned the solution a brown-yellow color. The solution was vigorously stirred for 2 more minutes and then stored at 25°C.

To make nanorods, a seed is required to work from. This solution prepares small gold nanospheres in such a way that rod formation is favorable. The literature explains that CTAB binds preferentially to a face on the gold and consequentially hinders growth in that direction, leaving only one axis open to growth. However, beginning from a mostly spherical shape, it is unclear how CTAB promotes rod formation. $NaBH_4$ is a reducing agent that reduces the gold from Au^{+3} to neutral elemental gold.

Growth Solution: In a new vial, 5 mL of .20 M CTAB was mixed with 40 μL of .016 M $AgNO_3$ at room temperature. 5 mL of .0010 M $HAuCl_4$ was added to the solution and gently mixed. Then, 90 μL of .08 M ascorbic acid was added to solution, turning it colorless. This solution was then heated to slightly above room temperature (27–30°C) and 12 μL of the seed solution was added. After a few minutes, a pale pink color indicates rod growth beginning.

The nanorods formed best when everything was freshly prepared. The seed solution is best used within a couple of hours after it is made. Nanorods can be characterized by their aspect ratios. This is the ratio of their length by their width. Our rods had an aspect ratio a little bigger than three.

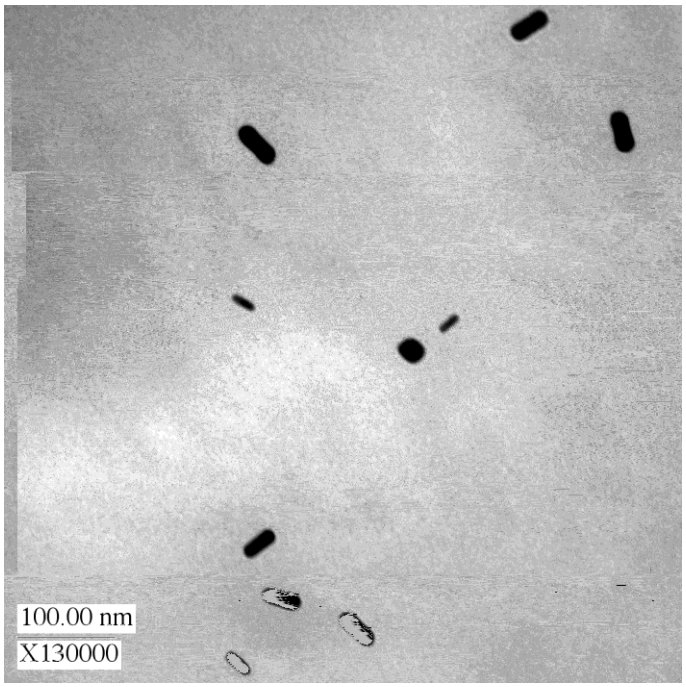


Figure 4: Transmission electron microscope (TEM) image of gold nanorods of length approximately 50 nm and width 16 nm.

Metamaterials can be tuned to different wavelengths by changing the aspect ratio of the rods within the design so it is important to synthesize rods with different aspect ratios. To increase the aspect ratio we used the same procedure for the seed solution and changed two additions in the growth solution. The original procedure calls for 40 μL $AgNO_3$ and 90 μL of ascorbic acid. We instead added 75 μL of each, keeping the concentrations the same as already described. This produced better aspect ratios (5:1), however, the solution was not as uniform, producing spheres as well as rods.

Figure 5: TEM image of nanorods with aspect ratio 5:1 mixed with nanospheres.

IV. Nanoparticles in Liquid Crystals

Although we are still working on perfecting the synthesis of nanorods to get better aspect ratios and uniform materials, we did dope some liquid crystals with nanorods. For the most part the first results were aggregation. We were able to introduce gold nanorods

into a hexagonal liquid crystal made of, by weight, 25% CTAB, 5% benzyl alcohol, and 70% water. All other phases of liquid crystals attempted (another H_1 (hexagonal) phase, a cubic and nematic phase) showed aggregation. To show with more confidence that there was no aggregation in the hexagonal liquid crystal we needed to image it, specifically with the TEM. Liquid crystals, however, cannot just be placed in the TEM the way a dried drop of nanoparticles can.

To image liquid crystals in a TEM, the liquid crystal must be frozen and then sprayed with metal. This procedure is called a freeze fracture. The liquid crystal is put into liquid propane. Propane is more thermally conductive than nitrogen and freezes the liquid crystal faster then nitrogen would. By freezing the crystal fast, we can be sure the crystal is in the phase we originally observed it and did not change in the cooling process. The liquid crystal is then transferred to liquid nitrogen, which cools the fracturing device, and placed within the fracturing device. We split the liquid crystal (fracture it), by two possible methods. One method uses a knife to cut the liquid crystal in half and the other method splits the liquid crystal by quickly opening a glass cell. The pictures below used the knife fracture technique. We spray the split crystal with a thin sheet of platinum. This metal maps the surface of the liquid crystal. The metal covering is then separated from the liquid crystal by simply dissolving the liquid crystal away. The remaining metal map can be put into the TEM. We preformed a freeze fracture on our sample and then observed it in the TEM.

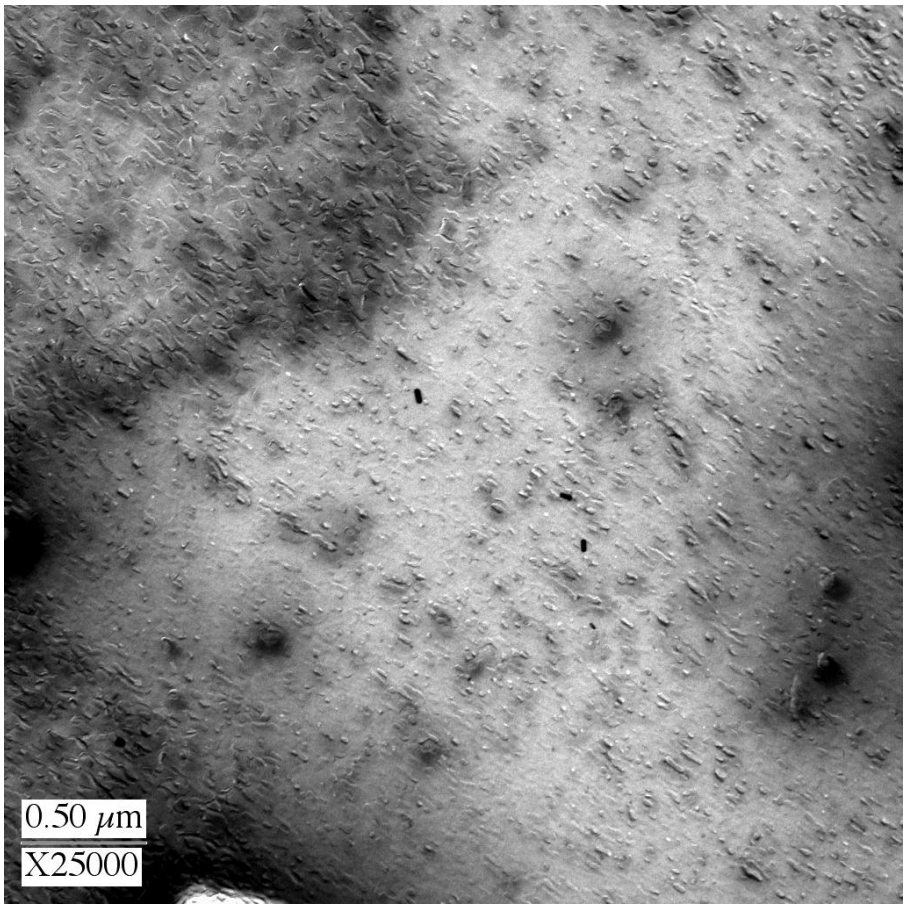


Figure 6: A hexagonal phase liquid crystal with nanorods.

There appears to be some orientation along the northwest-northeast diagonal. The next picture is of the same area but of a higher magnification.

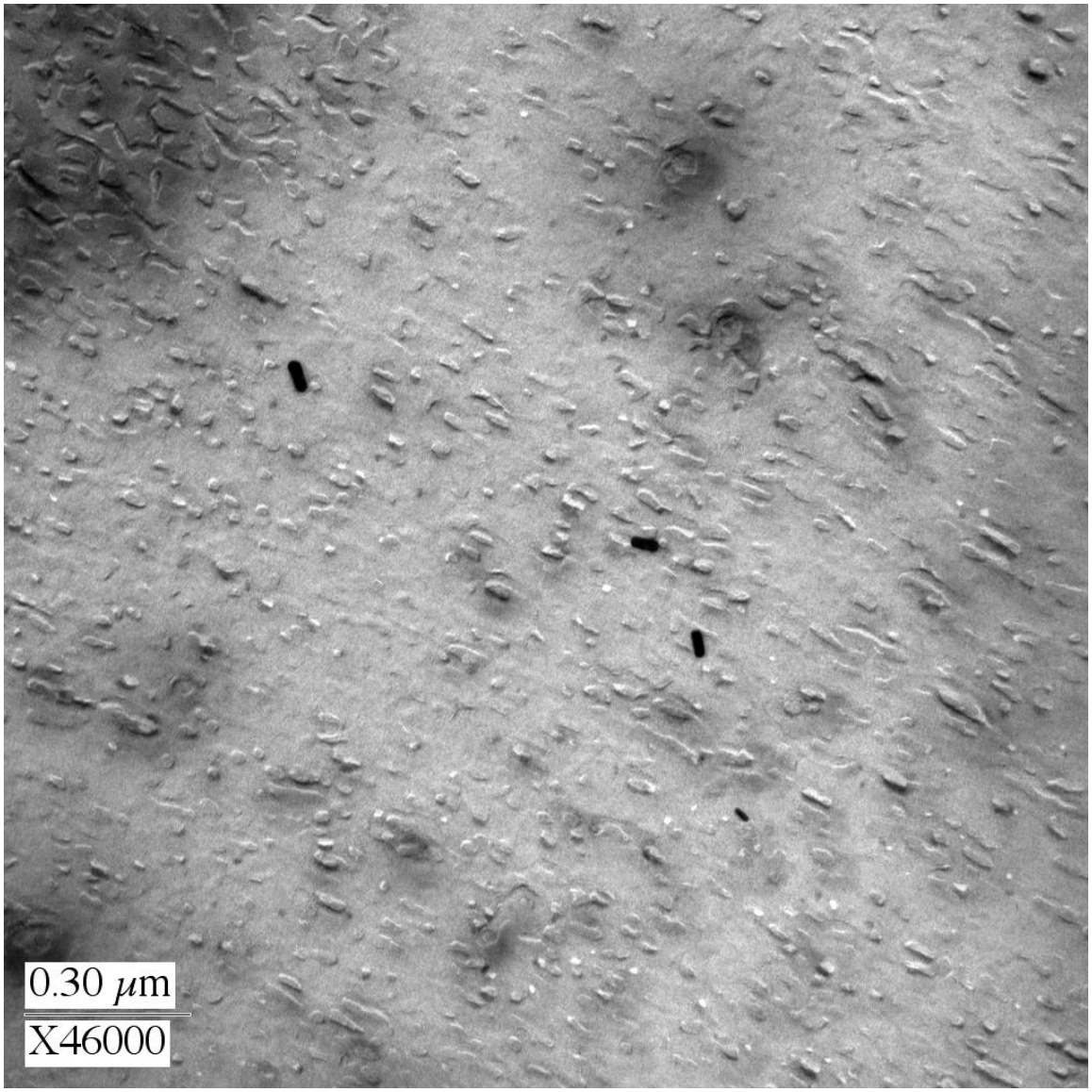


Figure 7: A higher magnification of Figure 6. Hills suggest nanorods assembled into long-range orientation.

At this resolution it appears that some of the "hilly" features are the same size as the dark nanorods. This suggests that nanorods were aligned in the liquid crystal. There are three very visible dark rods because they are stuck to the metal layering. Most rods did not stick. We know this because when only considering the very visible rods, this picture does not accurately represent the concentration of nanorods put in the crystal. These hills show long-range orientation, suggesting the nanorods have self-assembled into long-range orientation along the diagonal.

As mentioned before, more than one phase and type of liquid crystal was attempted but the other attempts showed aggregation. Nanoparticles are small enough such that they are uniformly suspended in solution; gravity is negligible. The Van Der Waals force causes the gold nanoparticles to attract one another. If the nanoparticles are not coated with a substance to prevent the particles from touching, the particles will aggregate. Once nanoparticles aggregate, they are no longer nano. The clump is often visible to the eye and they lose their nano properties. They, also, cannot be separated. CTAB not only helps rod formation but also prevents aggregation by acting as a buffer between nanorods. CTAB has a 16-atom chain of carbon atoms, which hinder other gold molecules from aggregating. However, when put into liquid crystals, CTAB no longer protected the gold well enough. The CTAB failed because the bond between the gold and the ammonium was not strong enough. We found it has been reported in the literature that thiol strongly bonds to gold. In an attempt to avoid aggregation in liquid crystals, we synthesized thiol capped gold nanospheres.

The paper we followed asked for tetraoctylammonium bromide to be dissolved in toluene. We did not have this compound on hand so instead used a similar compound, didodecyldimethylammonium bromide (DDAB). Because DDAB is smaller than the compound asked for, we increased its concentration by two.

Thiol capped gold synthesis: Dissolve 162 mg DDAB in 4 mL toluene. Add 1.5 mL of .03M gold solution ($HAuCl_4$) and stir. After the phase transfer is complete (an hour to two hours) pipette off the organic layer into a new vial. While stirring, add 10 μL of dodecanethiol and 1.25 mL of freshly made batch of .4 M $NaBH_4$ to the organic phase. After stirring for three hours, the solution was evaporated and washed with ethanol to remove excess dodecanethiol.

After preparation we looked at these nanospheres in the TEM and it became clear they were quite concentrated and yet still had not aggregated. The TEM shows they are about 1–3 nm in diameter.

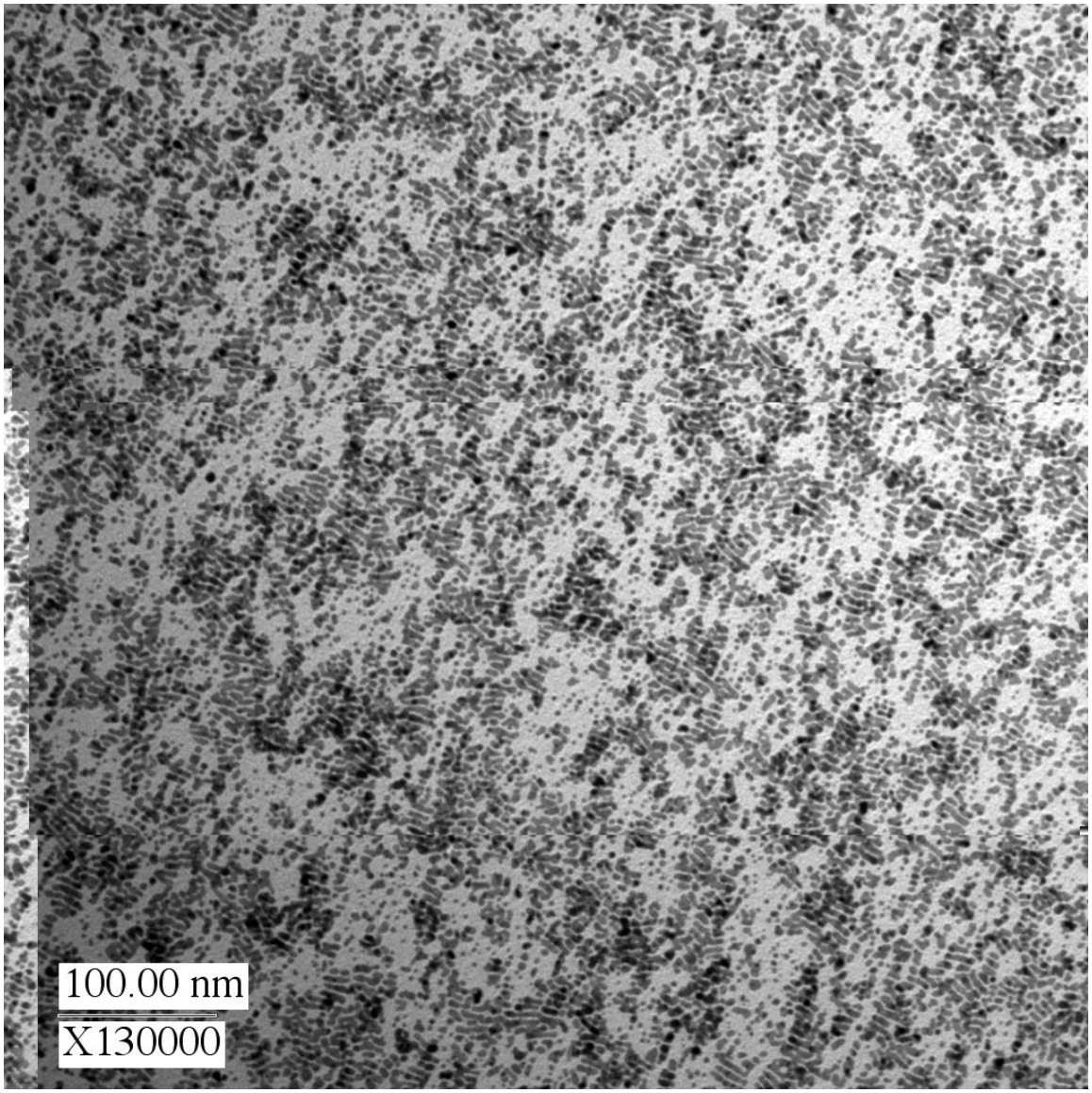


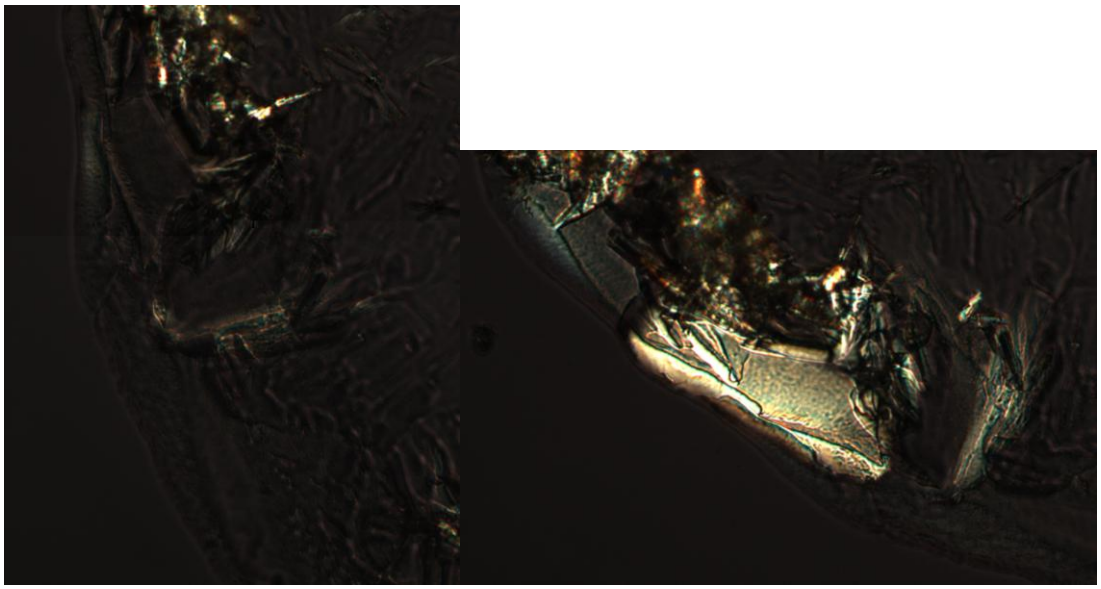
Figure 8: Dodecanethiol capped gold nanospheres 1-3 nm diameter.

The lack of aggregation in such a concentrated sample led us to try the thiol-capped spheres in four different liquid crystals. We tried two H_1 (hexagonal) phases: one liquid crystal was made of, by weight, 28% CTAB and 72% water, and the other hexagonal phase consisted of, by weight, 25% CTAB, 5% benzyl alcohol, and 70% water. A nematic liquid crystal, made of 12 mg sodium decyl sulfate (SDS), 2.3 mg decanol, and 16 mg water, was used. As well as a cubic phase liquid crystal made of, by weight, 43.7% DDAB, 7.2% styrene and 50.1% water. Preparation of liquid crystals requires centrifugation and then sonication of the sample. Each liquid crystal was made with 2 μL nanospheres. All samples, except for the hexagonal phase made with benzyl alcohol, rejected the nanospheres. Black clumps were visible and the purple color of the nanoparticle solution was no longer visible. The liquid crystal made with benzyl alcohol appeared to have accepted the nanospheres. We added more (2 μL) thiol capped spheres and again found no signs of aggregation present.

This work led us to look for ways to cap rods with thiol. Spheres in liquid crystals are moderately interesting because they have not aggregated. Spheres are limited by their geometry; they have the same dimension in every direction. The only possible alignment is in one dimension. In the literature we found papers on rods prepared in CTAB as we have done before and then transferred to an organic phase with dodecanethiol used as the new capping agent. All our attempts resulted in aggregation within the organic phase.

As mentioned earlier, nanoparticles are made of many materials. After the thiol capped nanorods failed, we needed to find and synthesize rods with a sufficiently strong capping agent. We turned to silver. Many papers have been published about silver nanorods because silver can give much bigger aspect ratios than gold. We have not yet been able to successfully make a solution of monodispersed silver nanorods. We are still working on the synthesis.

We have also been able to show alignment of nanorods in thin solid films. We obtained these films by drying a droplet of CTAB solution with nanorods. As the droplet dried, the CTAB and rods were concentrated at the edges. CTAB and water forms a liquid crystal phase. When this phase occurred during drying, the nanorods were aligned within in that domain and remained aligned after the droplet had completely dried. This can be observed by placing the domain under cross polarizers. If there is angle dependence on the amount of light let through, nanorods are aligned.



Figures 9 and 10: These pictures were taken 45 degrees apart under cross polarizers. There is a clear change in the amount of light let through dependent on the angle.

This can also be observed and confirmed by doing a plasmonic resonance absorbance spectrum of the droplet at different angles under polarized light. Nanorods have two dimensions that absorb different wavelengths of light: their width and their length. The width is the smaller length and will absorb a smaller wavelength of light than that of the length. Nanorods can be characterized by their absorbance spectrums because the longer the rods are the bigger wavelengths they will absorb. If the droplet shows angle dependence in the absorbance under polarized light, this implies there are aligned

nanorods within that domain. Below are our spectra showing angle dependence. We are still working on ways to make these spectra clearer and with less noise.

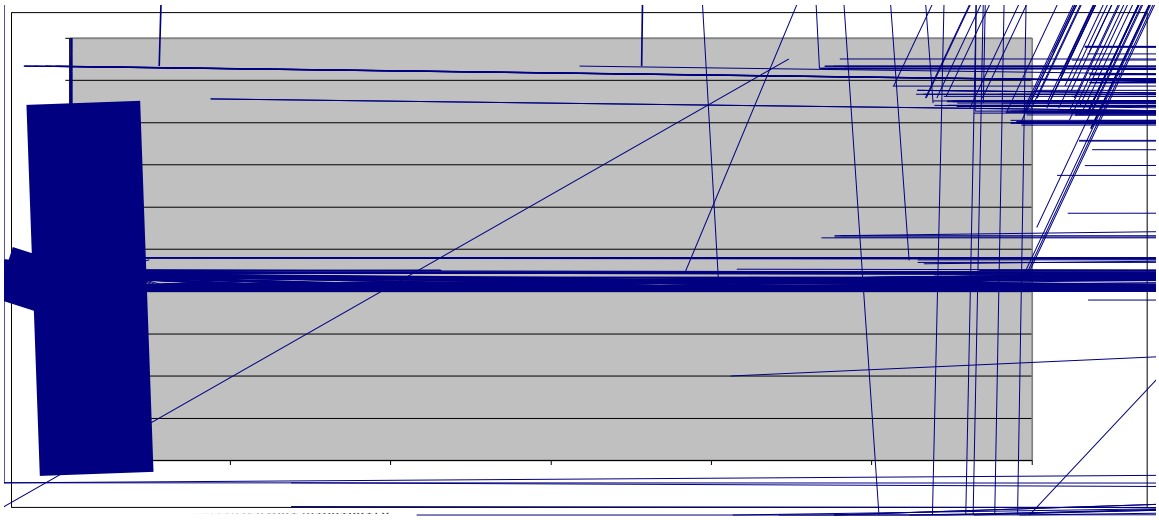


Figure 11: Plasmonic resonance absorbance spectra of dried droplet domain. The y-axis is light intensity and the x-axis indicates the wavelength of light being absorbed.

V. Conclusions

We have successfully put nanorods into a hexagonal phase of liquid crystal. We have also aligned nanorods in a thin solid film. We will work on perfecting the plasmonic resonance absorbance spectra of the thin solid films.

We will continue to make and refine the syntheses to get better monodispersed nanorods of both gold and silver. We will also look into some other nanoparticles of different shapes. One of our more recent attempts to synthesize gold nanorods instead produced nanodogbones, which have been previously reported in the literature.

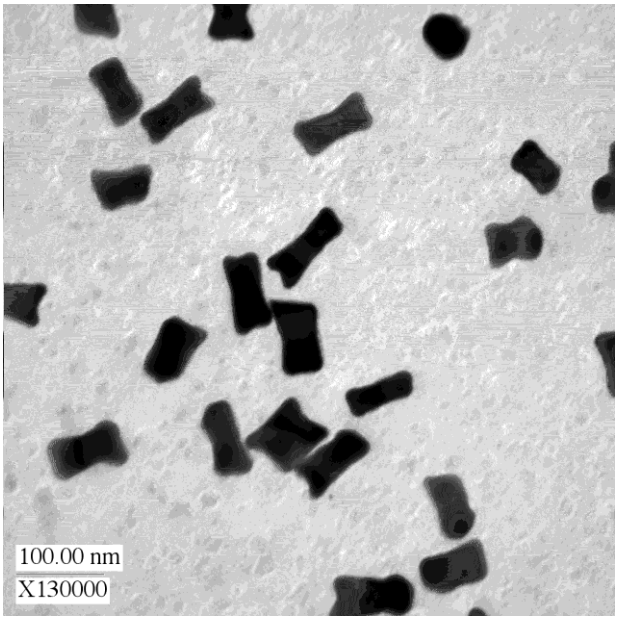


Figure 12: TEM image of gold nanodogbones.

Some metamaterials require two nanorods fused together along their length. Our nanodogbones resemble this design and we will be looking into this more closely on ways to possible use these nanodogbones.

We have tried in the past to put nanorods into cholesteric liquid crystals but have only seen aggregation. We will in the future keep looking into ways to prevent this aggregation. Cholesteric liquid crystals have a twisting structure as described earlier. Some metamaterials have rods aligned in a twisting structure. We are also looking into cholesteric liquid crystals because DNA forms a cholesteric liquid crystal when concentrated and we hope to eventually be able to put nanorods into DNA liquid crystals without aggregation.

In summary, we have been exploring conditions that favor the organization of nanoparticles in liquid crystals. By taking advantage of the natural organization of the latter, structures can be made from nanoparticles that may have novel optical properties. These may be useful for microscopy, material science, and medicine.

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