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Control of 1,4-Anthraquinone Crystal Growth

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CONTROL OF 1,4-ANTHRAQUINONE CRYSTAL GROWTH

by

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Quinones are widely found in nature, used in chemistry and medicine, and are just beginning to gain importance in materials engineering. In order to harvest their potential as an ordered or highly crystalline solid, their crystal formation processes need to be well investigated and controlled.

We chose 1,4-anthraquinone, a commercially available type of quinone, as a model compound to study its crystal growth behavior. These crystals were deposited through evaporation of a solution containing the anthraquinone and were subsequently studied through microscopy and various other methods. The effects of solvent variation, temperature, and impurities on crystal growth were all explored.

Control of the anthraquinone crystal growth was partially demonstrated. Poor solvent will discourage crystal growth, high temperatures promote a transformation of needle-like growth to plate-like growth, and butylated hydroxytoluene that are included in solvents will form coral shaped superstructures on the quinone.

These observations show the complexity and promise that quinones, 1,4-anthraquinone in particular, have enjoyed.

ACKNOWLEDGEMENTS

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A special thanks needs to go to Dr. Jinyue Jiang, for his immeasurable support and aid with experiments and research throughout my thesis work. Thank you also to Dr. Ziguang Chen for his help and advice with experiments and thesis advice.

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Chapter 1 Introduction

Quinones are a widely found and used family of aromatic compounds. Quinone's basic structure is that of one or more unsaturated carbon rings, with two carbonyl groups attached to the same or different rings.[1-5] A few simple quinones are sketched in Figure 1.1. Simple quinones like this are named based on the compounds they are derived from. For instance, anthraquinone is derived from the oxidation of anthracene, benzoquinone is derived from benzene, and so on.[6]

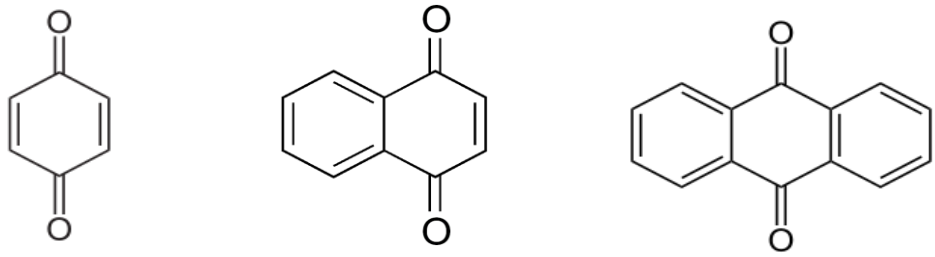

Figure 1.1: Chemical structure of benzoquinone, naphthaquinone, and 9,10-anthraquinone, respectively

Quinones can be found in all forms in plants,[2,7] animals,[8,9] insects,[10,11] humans,[12,13] and even as pollutants in the atmosphere.[14,15] With such a large range of exposures, it is important that quinones be understood, especially in how they can affect people as well as be applied in engineering to improve our living conditions.

In fact, quinones have been used extensively by humans for thousands of years, mostly in the form of plant extracts such as aloe or henna.[2] These uses, however, are simply taking advantage of natural products that happen to contain quinones. More recently, in the past century, quinones have become a focus in the scientific.

One of the main fields that quinones are investigated in is the compound's ability to work as an electron transporter.[1,2,16] They have been discovered to have a role in the degradation of matter and pollutants, by shuttling electrons to microorganisms in a reduction cycle.[17] In a similar process, azo dyes have also been shown to be reduced more effectively under the presence of quinones.[18,19] However, the most widely researched and applied area is that of medicinal uses. These compounds are found in antibiotics, vitamins, medications, and anticancer therapy.[1,2,16] Unfortunately, the same process that makes quinones an effective tool in the fight against cancer can create free radicals that can other toxicity, especially to the liver.[1] The fact that quinones are so prevalent in cancer research is yet another reason they deserve as much research time and energy as possible, as any new knowledge will benefit the medical field.

While the studies are not as extensive as in the medical field, quinones are also considered valuable compounds in the area of materials engineering. Dopaquinone, for instance, has been used as the basis of a multi-functional coating inspired by mussel biology, shown in Figure 1.2, which allows for adhesion to multiple surfaces.[20]

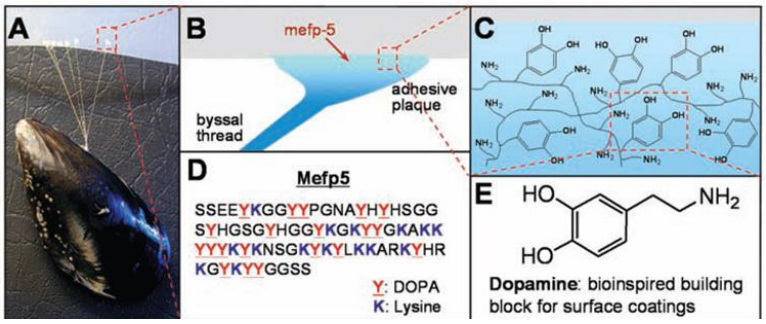

Figure 1.2: Inspired by mussel biology, dopaquinone has been used to form multifunctional coatings.[20]

This showcases quinones' abilities to interact with other compounds. Another interesting avenue of materials study, which directly pertains to this thesis, is the study of quinone crystal growth, especially that of anthraquinone. Anthraquinone readily forms crystals, whether through complicated techniques such as the Bridgman technique, evaporation, or precipitation of a saturated solution.[21-23] The type of crystals formed depends on the technique used, where bulkier single crystals are formed with the Bridgman technique, while needle-like crystals were observed from the vapor phase, seen in Figure 1.3.[21-23] This has paved the way for people to study them further without relying on sophisticated equipment.

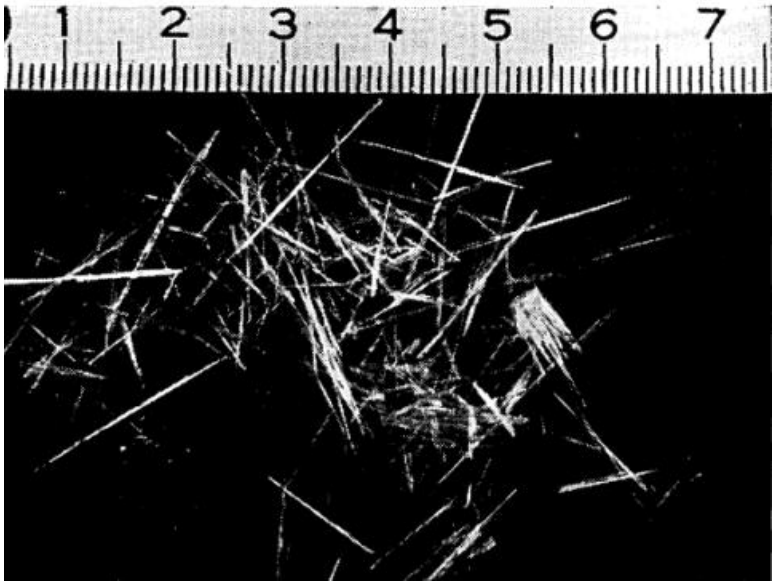

Figure 1.3: Needles of 9,10-anthraquinone.[22]

Of particular interest, and a driving force behind this research, is the possible use of anthraquinone as a building block in metal-organic frameworks (MOFs). MOFs are lattice-like compounds with vast internal surface area due to their unique structure.[24,25] This large surface area makes MOFs ideal candidates for trapping and storing gases.[26] 1,4-anthraquinone can be used in conjunction with inorganic salts to form an organic-inorganic hybrid polymer potentially

capable of carbon capture. Since the carbonyl groups from the 1,4-anthraquinone have a tendency to build a tight band structure with surrounding metal elements, further adsorption of gases will interrupt such a trend by delivering a strong color change, essentially signifying the presence of carbon.[27] Understanding the structures that 1,4-anthraquinone forms on its own is paramount in understanding how to apply the structures formed when it reacts with inorganic salts. Once successful, it can not only be applied to the specific area of materials science, but also suggests great application of other quinone based compounds.

Overall, due to the growing interest in using quinones in materials research, and the already extensive examples in biological and medical fields, there is a need to understand how quinone crystals are formed. Beyond simply understanding the structures, controlling the types of crystals formed will shed light on any prominent future engineering applications.

Chapter 2 Control of 1,4-anthraquinone Crystal Growth

2.1 Materials

Pure 1,4-anthraquinone was purchased from Alfa Aesar and was used as received. Stock tetrahydrofuran (THF) was purchased from Sigma Aldrich. It is >99% pure, containing 250 ppm of butylated hydroxytoluene and was used as received. Silicon wafers (500 µm prime grade 4 in, P(100) 10-20 ohm-cm SSP and P(100) 1-10 ohm-cm DSP) were purchased from University Wafer. Windex®, ethanol, and acetone were used as solvents to clean the wafers. Dried tetrahydrofuran was received from the University of Nebraska-Lincoln Chemistry Department and used as is. Pure butylated hydroxytoluene was purchased from Sigma Aldrich, and was used as received. Crystalline samples prepared by the following experiments were examined with a Meiji ML8000 optical microscope with a Moticam2000 digital camera, a Nova NanoSEM450, Hitachi S4700 Field-Emission SEM, and a Bruker Avance 400mhz NMR.

2.2 Methods

Experiments were performed in three distinct areas: interaction with water, temperature dependence, and interactions with organic impurities. Detailed procedures are described below.

Interaction with Water

Five solutions containing various amounts of 1,4-anthraquinone and THF were prepared in 20 mL glass vials. Tetrahydrofuran was added to the vial using a needle and syringe, and deionized water was added subsequently, also with a syringe. The total amount of liquid is kept at 5 mL, while the percentage of water varied from 0% to 50%. Table 1 shows the amounts of each constituent added.

Table 1: Solutions of 1,4-anthraquinone with varying amounts of water

Sample	Grams of Anthraquinone Added	Percent of Water (by volume) in Solution	Molarity of Final Solution
TH-55-01	0.0164	0%	15.8 E -3 M
TH-55-02	0.0125	2%	12.0 E -3 M
TH-55-03	0.0140	10%	13.4 E -3 M
TH-55-04	0.0142	20%	13.6 E -3 M
TH-55-05	0.0135	50%	12.9 E -3 M

After solid and liquid addition, each vial was sonicated for 5 minutes to ensure a complete dissolution of the solid. A silicon wafer approximately 1 cm square was wiped with Windex®, ethanol, and acetone, respectively, and allowed to air dry in between cleanings. The wafer was then placed at the bottom of those vials containing the 1,4-anthraquinone, with the shiny side of the wafer facing up. Each vial was then placed in the laboratory fume hood, uncapped to let the liquid evaporate overnight. Once the liquid was removed, the wafers were carefully removed using tweezers. Each sample was analyzed with a Meiji ML8000 optical microscope equipped with a Moticam 2000 digital camera. The digital camera also includes image-analysis software to determine scale size for each picture.

In addition to those crystals grown inside glass vials, the effect of water on crystal growth was also investigated by placing liquid droplets on a glass slide under the optical microscope. Specifically, a drop of the 1,4-anthraquinone solution in THF was pipetted onto a drop (~0.05mL) of deionized water that is already on the glass slide. The Moticam 2000 was used to take a picture every 30 seconds as the solution evaporated, to track the progress of crystal.

Temperature Dependence

0.0138 g of 1,4-anthraquinone were dissolved in 5 mL of THF and a clean silicon wafer was placed at the bottom of the vial. This vial was then immediately placed, standing up, in the

center of a wide mouth beaker (2000 mL in volume). Water was added to the beaker, around the vial, until it was level with the amount of 1,4-anthraquinone solution. This beaker was placed on a hot plate with a temperature of $160^{O}F$ and allowed to evaporate. The evaporation took place over approximately 45 minutes. Once the solution had evaporated, the silicon wafer was removed and the deposited crystals were examined under the Meiji ML8000 optical microscope. Additionally, scanning electron microscopy (SEM) was performed using a Hitachi S4700 Field-Emission SEM.

Another sample was prepared under the same procedure, using 0.0198 g of 1,4-anthraquinone and 5 mL of THF. The vial was again heated in a water bath at $160^{O}F$ as the solution evaporated. Once the silicon wafer was covered in a layer of crystal deposits, it was quickly removed from the vial and replaced with another clean silicon wafer. Each time a wafer was covered in crystal deposits, it was removed and replaced with a new, clean wafer. This was repeated until the solution had completely evaporated, for a total of four silicon wafers. Each of the four wafers was examined using the Meiji ML8000 and Moticam200. Additionally, the crystals from the second wafer were removed after microscopy to undergo nuclear magnetic resonance using a Bruker Avance 400mhz NMR. The specific settings used on the NMR are presented in Figure 2.1.

```
NAME      Tyler-plate-6-15-2012-THF-300M
EXPNO                  2
PROCNO                 1
Date_           20120615
Time                11.55
INSTRUM             spect
PROBHD   5 mm QNP 1H/13
PULPROG              zg30
TD                  32768
SOLVENT               THF
NS                    128
DS                      2
SWH              5995.204 Hz
FIDRES           0.182959 Hz
AQ               2.7329011 sec
RG                  574.7
DW                 83.400 usec
DE                   6.50 usec
TE                  298.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  10.00 usec
PL1                  2.20 dB
SFO1         300.1318534 MHz
SI                  32768
SF           300.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
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Figure 2.1: NMR Settings

Interactions with Impurities

Six samples were prepared using the same 1,4-anthraquinone that has been previously described. Three of these samples were dissolved in the stock THF (containing 250 ppm BHT as a radical inhibitor), while the other three were dissolved in dried and pure THF (received from the Chemistry Department of the University of Nebraska-Lincoln). In each set of three samples, deionized water was added in the concentration of 1%, 2% and 10%, as detailed in Table 2. These six vials were left, uncapped, to dry in the fume hood overnight to allow crystals to deposit on the silicon wafers. Surfaces of these six wafers were then analyzed using a Nova NanoSEM 450.

Table 2: Dry and Stock Solutions of 1,4-Anthraquinone

Sample	THF Used	Solution Volume	Percent of Water in Solution	Anthraquinone in Solution	Molarity of Solution
TH-68-01	Dry	5 mL	1%	0.0143 g	13.75 mM
TH-68-02	Dry	5 mL	2%	0.0135 g	12.98 mM
TH-68-03	Dry	5 mL	10%	0.0140 g	13.46 mM
TH-69-01	Stock	5 mL	1%	0.0153 g	14.71 mM
TH-69-02	Stock	5 mL	2%	0.0156 g	15.00 mM
TH-69-03	Stock	5 mL	10%	0.0150 g	14.42 mM

Another sample was prepared using the same procedure as above, with 0.0124 g of 1,4-anthraquinone dissolved in 5.0 mL of stock THF (250 ppm BHT). A clean silicon wafer was placed in the vial. The vial was left uncapped in the fume hood overnight for the solution to evaporate. Once crystals had deposited on the wafer, the wafer was removed from the vial and broken in half. One half was kept as is, the other was dipped quickly in dry THF. These two halves were then examined with the Nova NanoSEM 450 and compared to one another.

Three further samples were prepared using 1,4-anthraquinone (same as previously described), dry THF, and butylated hydroxytoluene (BHT). The anthraquinone and BHT were placed in the glass vial first, and then the same procedure for preparing the solutions was followed as before. The amounts of each constituent are detailed in Table 3. Once the silicon wafers were placed in the vials, the vials were left uncapped in the fume hood overnight, to allow the solution to evaporate. The deposited crystals were then examined under SEM using a Hitachi S4700 Field-Emission SEM.

Table 3: Samples prepared with dry THF and added BHT

Sample	BHT Added	1,4-Anthraquinone	Dry THF
TH-70-01	0.0045 g	0.0170 g	5 mL
TH-70-02	0.0026 g	0.0133 g	5 mL
TH-70-03	0.0057 g	0.0117 g	5 mL

2.3 Results and Discussion

Interaction with Water

Sample TH-55-01 (Figure 2.2), with no added water, formed many long uniform needles that were well attached to the substrate. These are the same type of needles generally found in the crystal formation of anthraquinone, and provide a good base of comparison for the rest of the samples. Some small plates did form, but the general composition was overwhelmingly needles.

In sample TH-55-02 (Figure 2.3), 2% water by volume was added to the solution, and again, needles formed predominantly. However, what can be described as a thin film of anthraquinone also formed on the plate, filling the areas around the needles. In some areas, this film took on the appearance of plates, providing a slightly higher amount of plates found when compared to TH-55-01.

Sample TH-55-03 (Figure 2.4) was made with a solution of 10% water by volume, and changed dramatically compared to samples -01 and -02. The crystals deposited in a dense thicket of small, overlapping needles. The needles formed a star-like pattern, with multiple branches growing out from a central point. It was hard to determine the presence of any plates due to the crowding of needles on the substrate.

In sample TH-55-04 (Figure 2.5), 20% water by volume was added to the solution. In this case, some long fine needles formed on the substrate. Most of the deposits found, however, were granular in nature, similar to the powdered anthraquinone originally dissolved in the THF. These deposited grains do not show any sort of crystalline structure.

In the final sample, TH-55-05 (Figure 2.6), a full 50% of the solution was water. This case carried on the trend of sample -04, in that the entire substrate was covered in a thick deposit of anthraquinone grains, rather than any specific crystal formation. These grains seem to be deposited with some order when considered on a larger scale, but do not show any of the characteristics of the needles or plates being examined.

In order to further understand the interaction between anthraquinone and water, a direct observation of anthraquinone crystallizing in water was performed. In this case, the anthraquinone formed small crystals as the THF evaporated, but these crystals were suspended in the water droplet, as the water did not evaporate as quickly. The suspended crystals flowed to the edge of the water droplet, and were deposited as the water evaporated, leaving groups of small crystals clumped together, as seen in Figure 2.7.

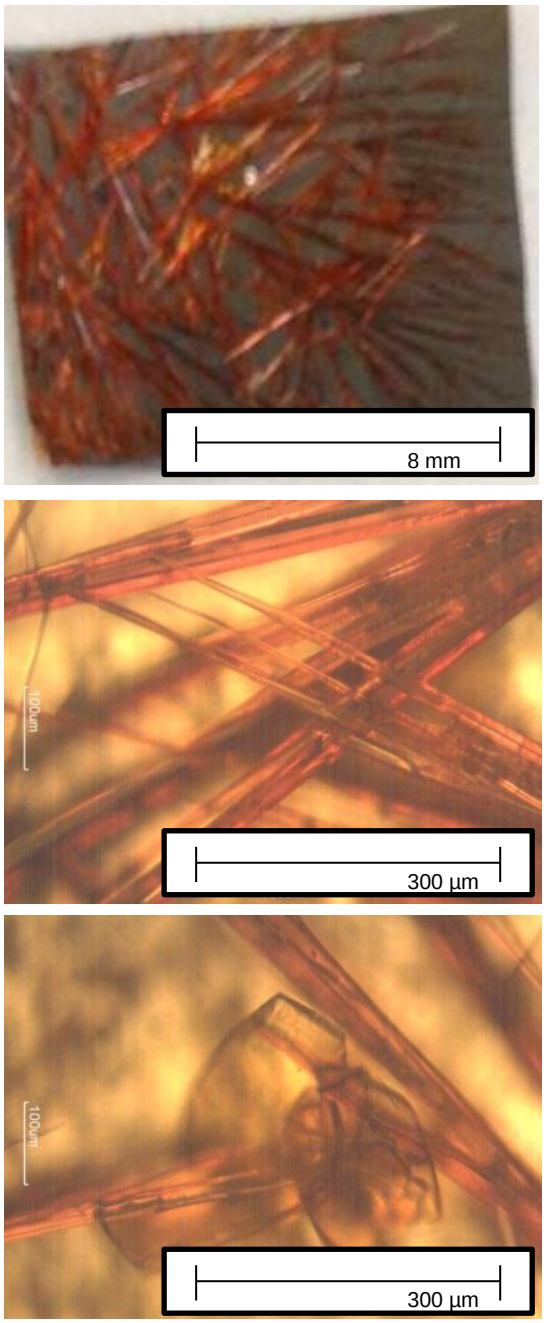


Figure 2.2: From top to bottom - Substrate covered with needles, Microscopic view of needles, Microscopic view of plates

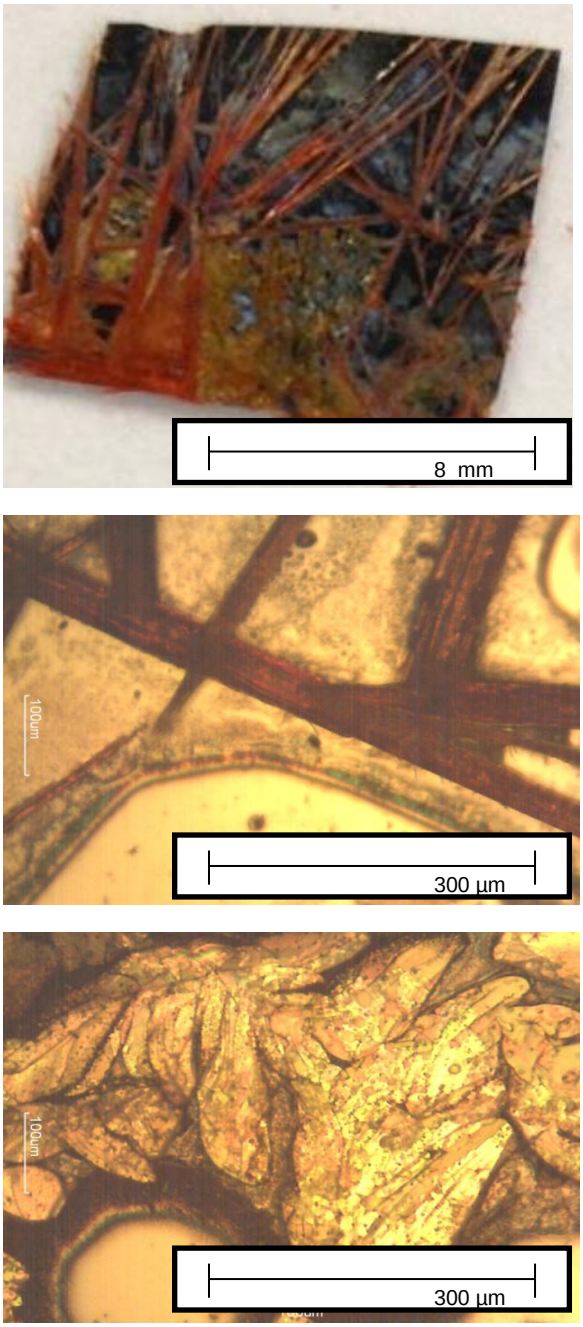


Figure 2.3: From top to bottom – Substrate with needles and anthraquinone film, Microscopic view of needles surrounded by film, Microscopic view of plate-like film.

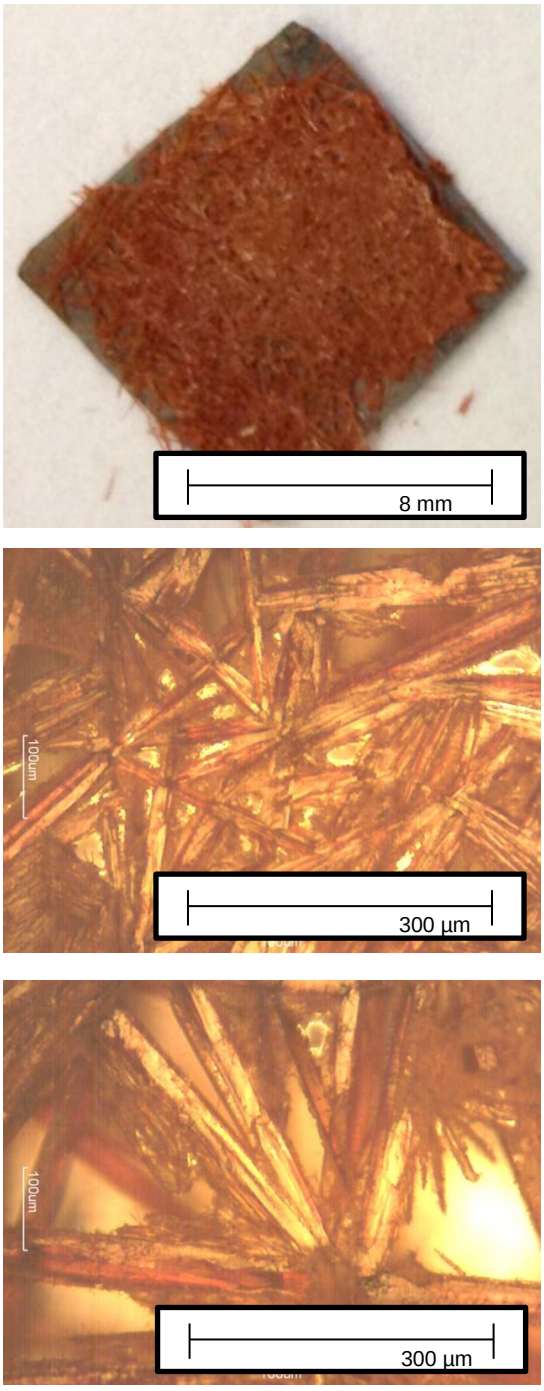


Figure 2.4: From top to bottom – Substrate covered in densely packed needles, microscopic view of needles overlapping, microscopic view of needles growing from center point

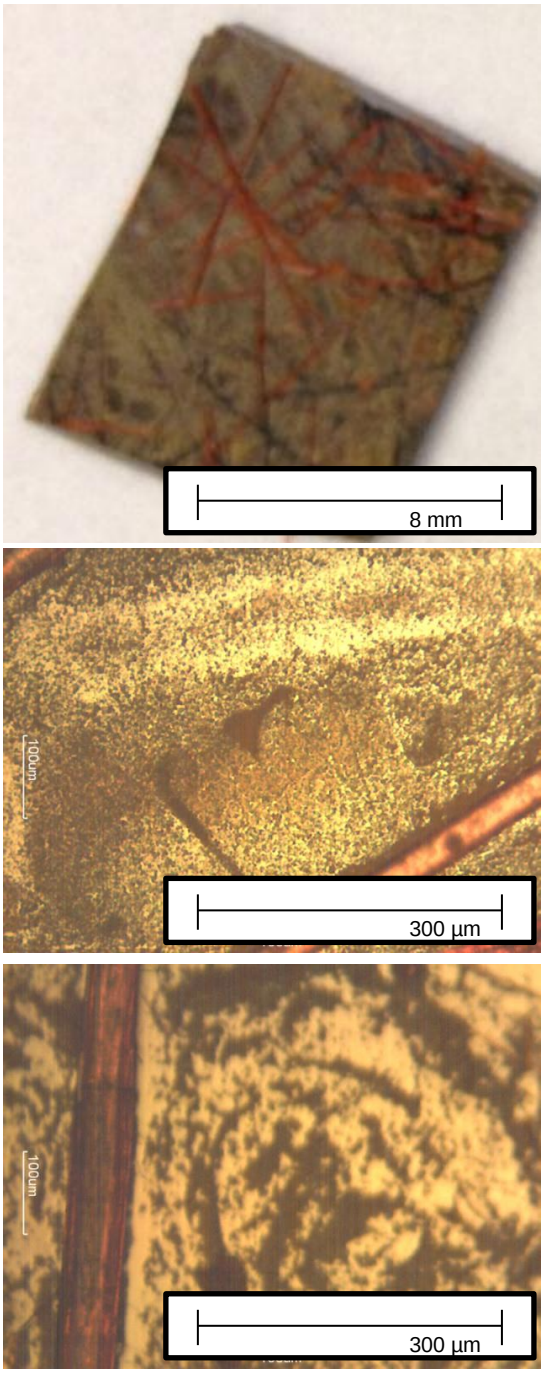


Figure 2.5: From top to bottom – Substrate with few needles and mostly grainy deposits, microscopic view of grains, enhanced view of grains

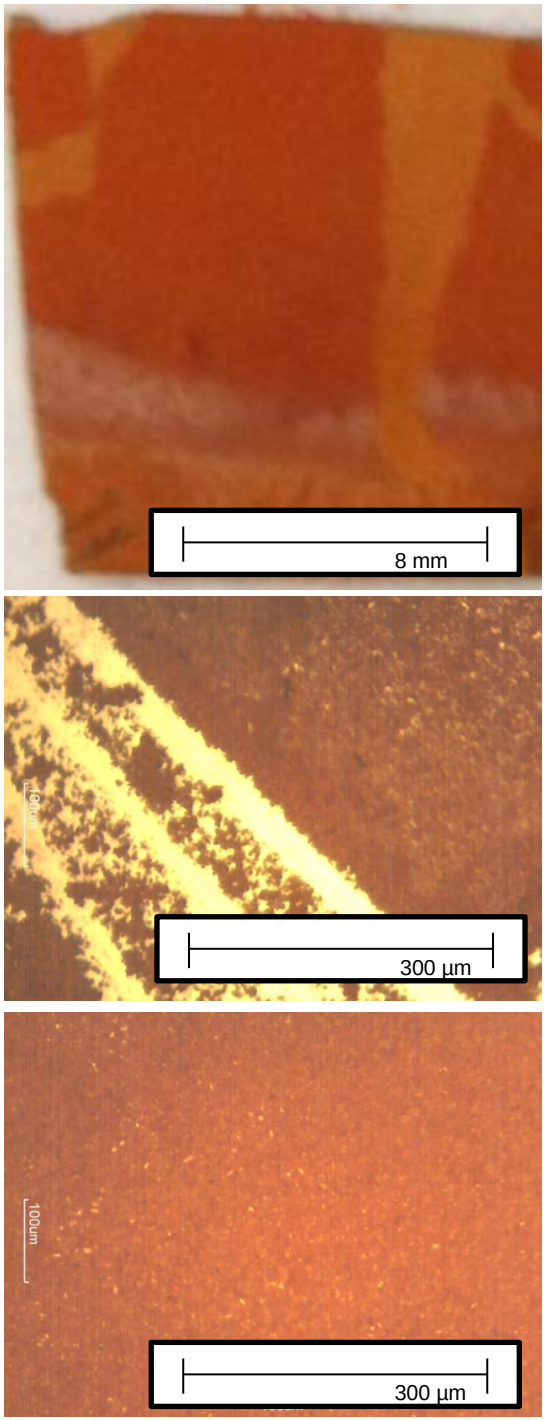


Figure 2.6: From top to bottom – Substrate covered in anthraquinone deposit, edge of deposits under microscope, surface of deposits under microscope.

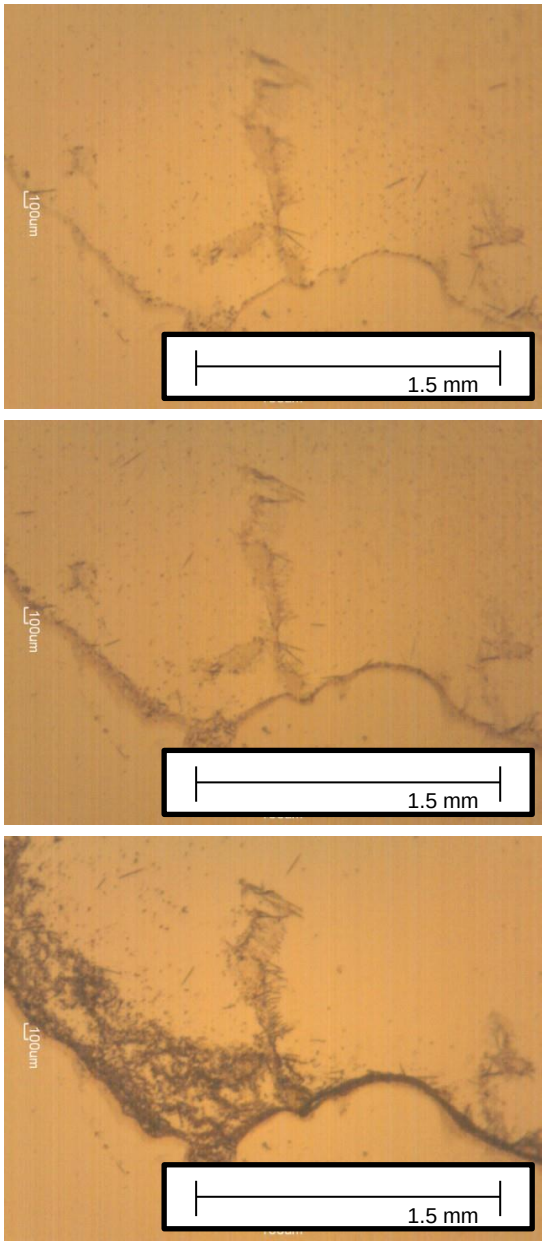


Figure 2.7: Anthraquinone crystals form as the THF evaporates, and are then suspended in water. As the water evaporates, formed anthraquinone crystals are deposited at the edge of the droplet. Shown sequentially over time from top to bottom.

Temperature Dependence

The addition of heat during the evaporation process resulted in a much quicker evaporation time than at room temperature, approximately one hour compared to eight or more, and the formation of many plates covering the entire substrate, seen in Figure 2.8. This high number of plates had not been observed previously, and the sample was subsequently analyzed more closely.

TH-58-04 was examined under both optical and scanning electron microscopes to determine its unique characteristics. Under the optical microscope, it was observed that the crystals formed were not only plates, but needles as well. The needles constituted the first layer of crystals on the substrate, and subsequent plates formed on top of these needles, as seen in Figure 2.9. Additionally, when viewed under the SEM, the quinone plates showed a basic structure of small finger shapes, much smaller than had been observed in the needles (Figure 2.10). These two observations, plates forming after the needles and the smaller building blocks that form the plates, seemed to indicate that the plates were formed by another compound besides anthraquinone, one with smaller molecules that would remain in solution longer, thus forming crystals after the anthraquinone had been deposited. From this observation, it became clear that the formation of these plates needed to be further analyzed to determine their composition.

In order to determine the make-up of the plates formed, they needed to be isolated from the anthraquinone needles. Once isolated and observed, it was determined what caused the plates to form in such a high number at a high temperature. A total of four wafers were prepared using the same solution in an effort to isolate the plates from the needles and examine them more closely.

Wafer 1 (Figure 2.11) was very similar to sample TH-58-04. It had a layer of needles formed on the substrate, and was covered in a layer of plates. Wafer 1 was analyzed under the optical microscope, but did not provide the isolated plates necessary for observation.

Wafer 2 (Figure 2.12) had much fewer needles, and was covered in mostly plates. It was estimated that only 10-20% of the crystals formed on wafer 2 were needles. Additionally, multiple instances were found of plates forming on the substrate with needles growing directly into and out of them, as shown in Figure 2.13.

Wafer 3 (Figure 2.14) was also covered in mostly plates, as expected. However, needles also formed, which was unexpected, as the hypothesis was that the plates would form after the needles. If this were the case, there should have been only plates on wafer 3.

Wafer 4 (Figure 2.15) was the final substrate to be used, and therefore not much of the solution was left to form crystals on the substrate. However, the crystals that did form seemed to be a combination of needles and plates, which is also unexpected, as it was thought that the needles and plates were separate elements, and should not be forming hybrid crystals.

Wafer 2 had the least amount of needles present on the substrate, and so had the most plates isolated on it. This wafer was selected to perform nuclear magnetic resonance (NMR) on, in order to determine the elements present in the sample. The top layer of crystals was scraped off of the wafer, in an effort to further isolate the plates from the needles that formed on the bottom layer on the substrate. The crystals were redissolved in deuterated THF, to ensure that the solvent did not affect the results of the NMR, and NMR was performed. The peaks found on the NMR (Figure 2.16) closely match those found for 1,4-anthraquinone (Figure 2.17, provided by Jinyue Jiang of the University of Nebraska).

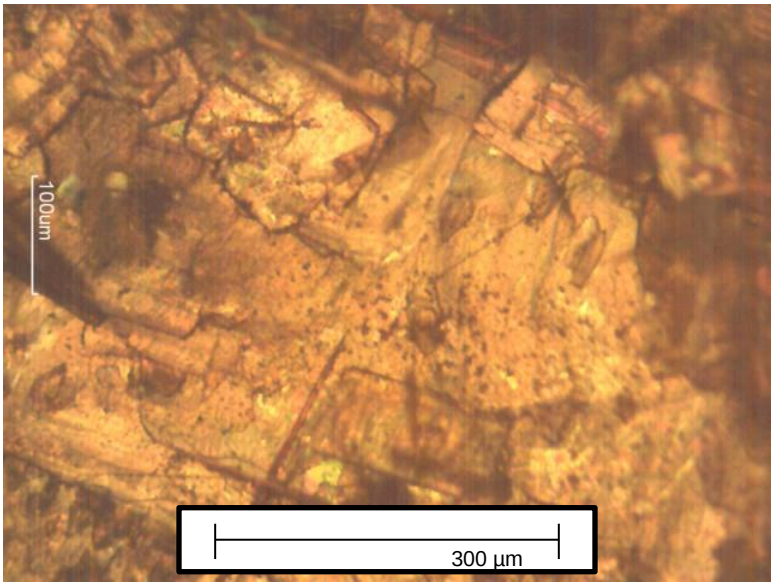


Figure 2.8: Flat, plate-like crystals formed after heating of the solution during evaporation

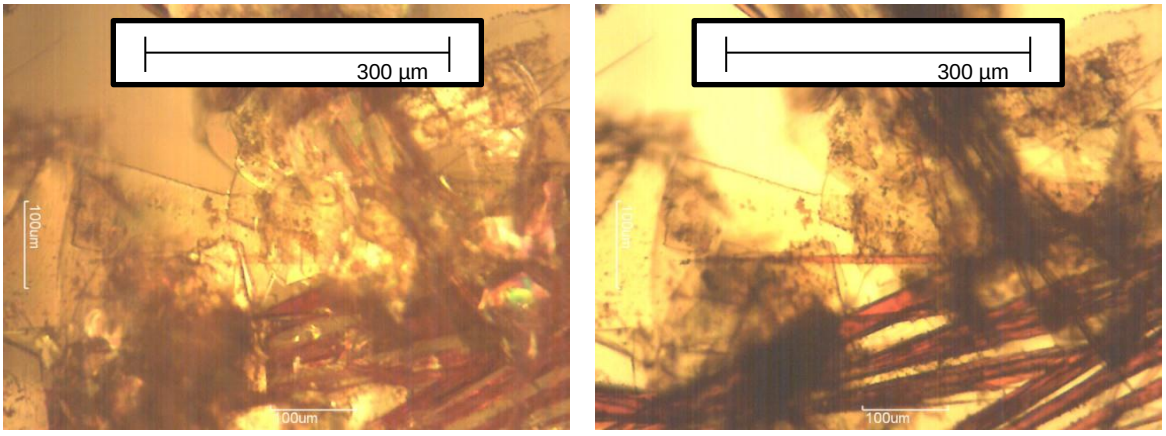


Figure 2.9: The left picture shows a portion of the substrate covered in plates. On the right, the same portion is lit from the underside, showing the layer of needles under the plates.

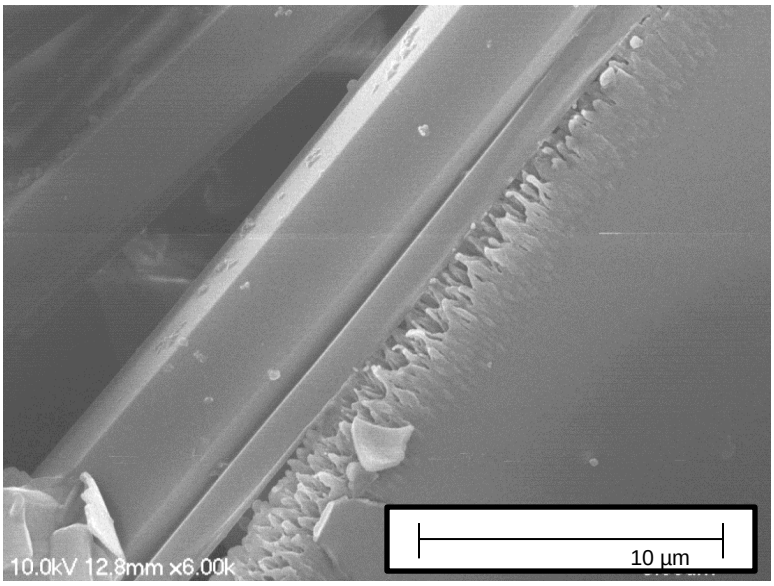


Figure 2.10: The same sample was analyzed under SEM. The edge of the plate, seen to the right above, is made up of small, finger-like growths, unlike the smooth needle seen on the left.

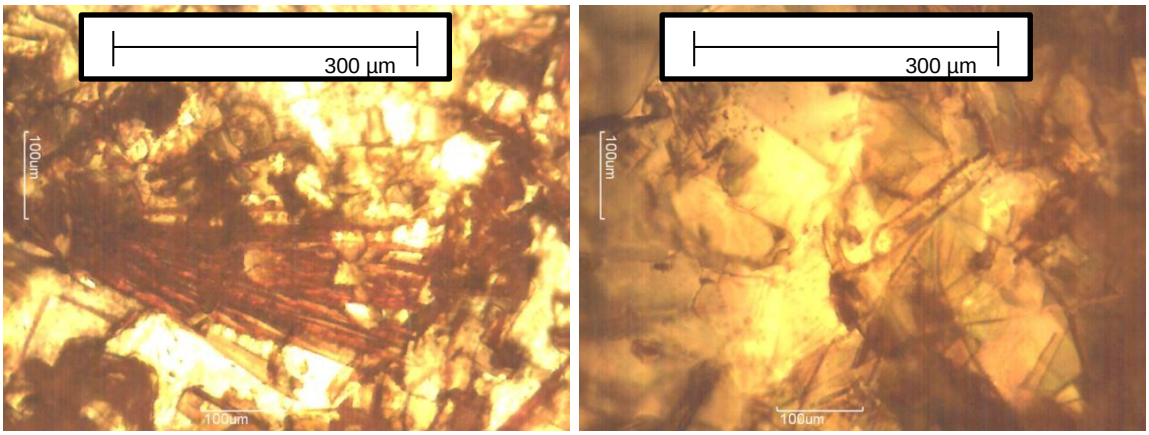


Figure 2.11: Wafer 1, with needles seen in the picture on the left, and plates seen in both pictures.

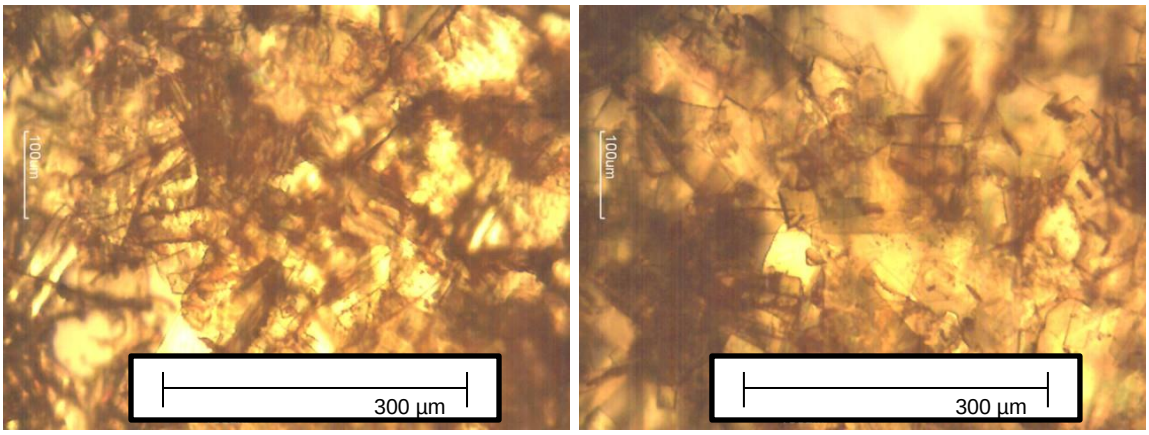


Figure 2.12: Wafer 2 had very high concentrations of plates, and not many needles.

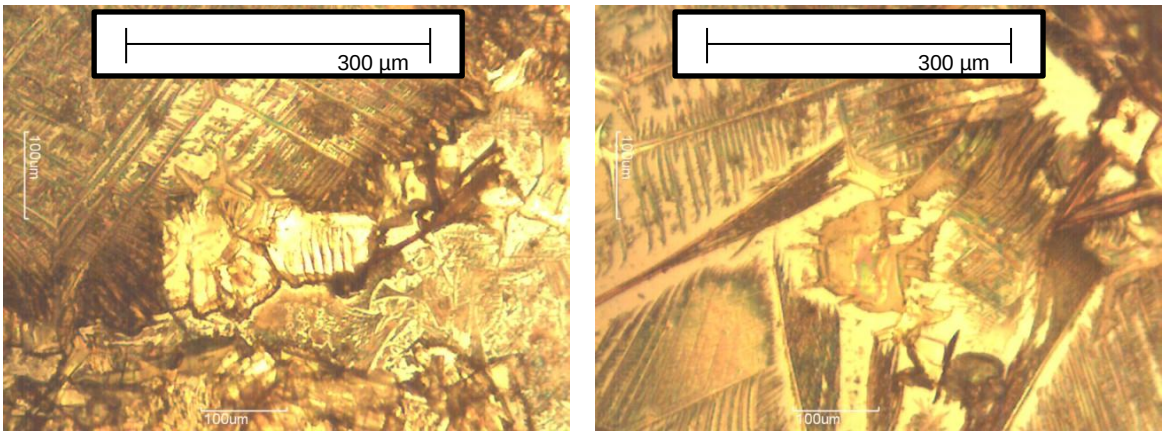


Figure 2.13: Examples of hybrid crystals seen on Wafer 2.

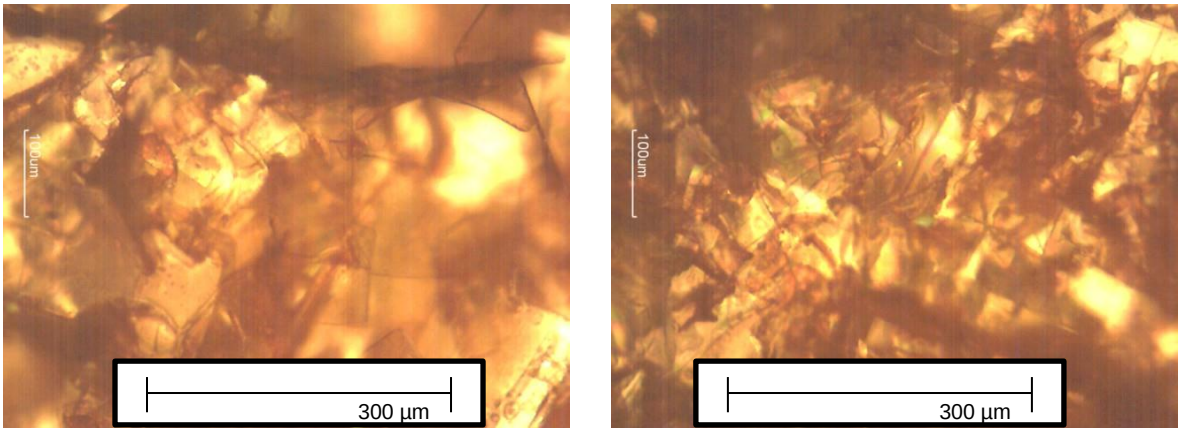


Figure 2.14: Wafer 3 had a high concentration of plates, but also contained more needles than expected.

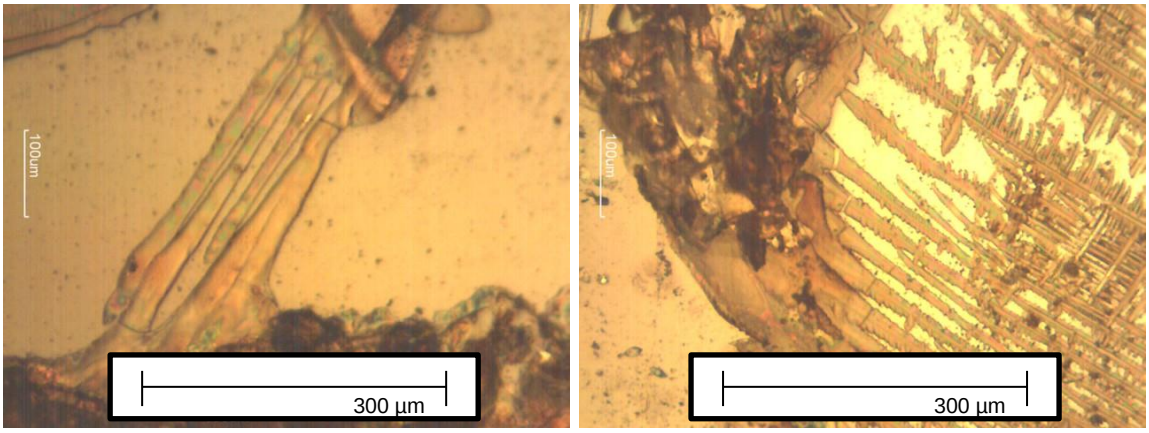


Figure 2.15: Hybrid needle/plate crystals observed on Wafer 4.

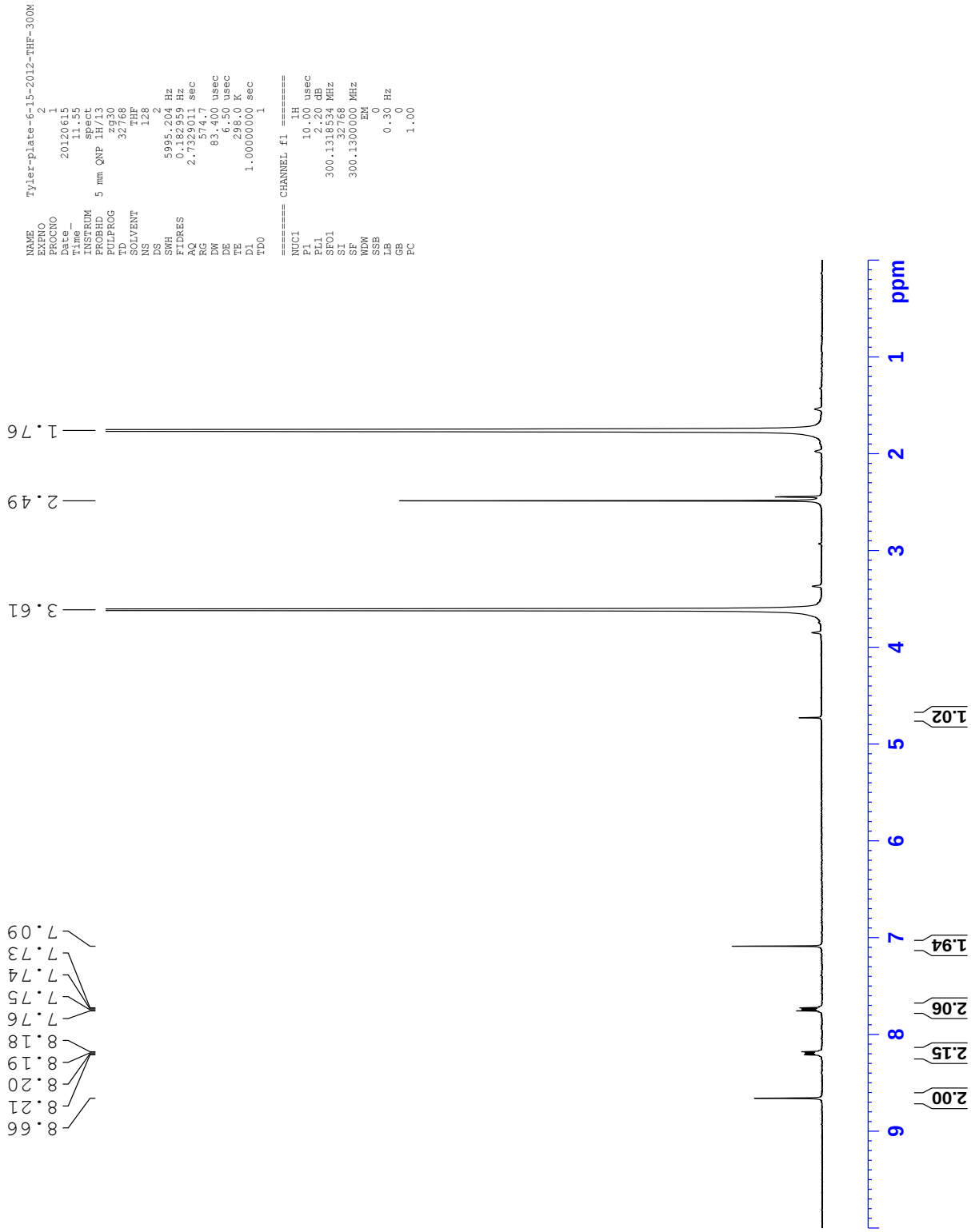


Figure 2.16: NMR results for the plates from the second wafer. The peaks between 7-9 ppm are a match of those seen for 1,4-anthraquinone.

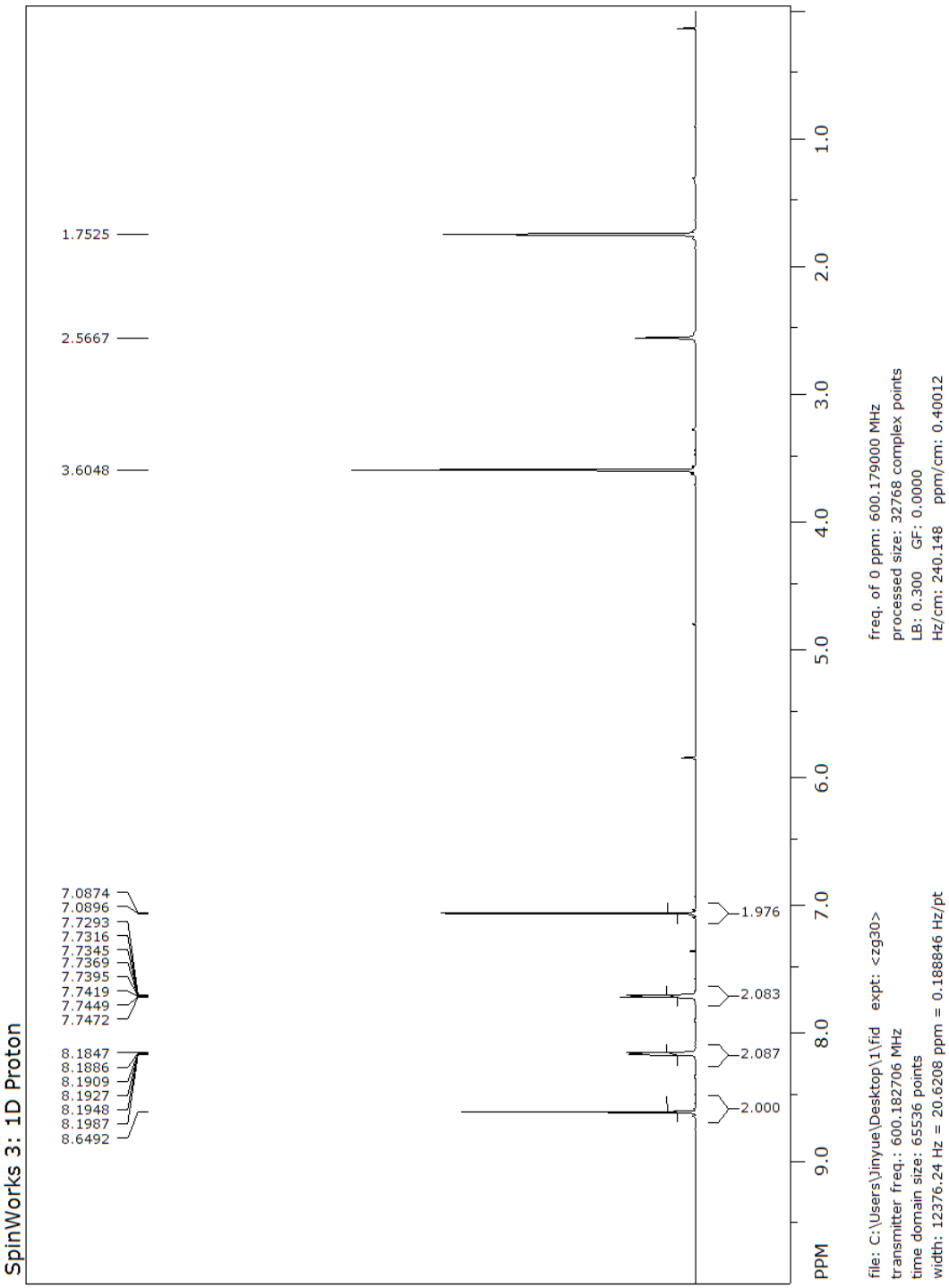


Figure 2.17: NMR results of 1,4-anthraquinone. This sample has peaks matching that of Wafer 2.

Interactions with Impurities

During preliminary observations of the anthraquinone crystals, some interesting growths were found on the surface of the solid anthraquinone formations. These growths had a different structure than the anthraquinone crystals, and looked like small hairs or coral formations growing out of the surface of the anthraquinone crystals. It was noticed that the new growths were absent on samples created with THF that had undergone a drying process (Figure 2.18), but were extremely prevalent on samples made using the stock bottle of THF (Figure 2.19). These unknown formations were hypothesized to be formed from the impurities in the stock THF, specifically butylated hydroxytoluene, or BHT. The BHT is added to the THF in the amount of 250 ppm, and is used as a stabilizer for the solvent. In order to test this hypothesis, samples were prepared using the stock THF, which included the BHT, and THF which had been put through a drying process to remove all moisture and impurities.

Three new samples were prepared using the stock THF as a solvent, and three samples were prepared using the dry THF.

Samples TH-68-01, TH-68-02, and TH-68-03 were all mixed with dry THF. Each sample was clear of any extraneous growth on the anthraquinone crystals. Sample TH-68-03 had raised craters on the surface of the crystals, but this can be attributed to deposition as the water evaporated, and does not match the growth of small hair-like structures being analyzed. Similar deposits, identified as coffee ring deposits, are being researched are being researched due to their simple mechanism of developing complex, ordered shapes under evaporation and flow conditions.[28]

The extra growths were clearly present in samples TH-69-01, TH-69-02, and TH-69-03. These three samples were made with a solution of the stock THF, which contains BHT. These observations support the hypothesis that the BHT interacts with the anthraquinone, forming smaller growths on top of the crystal structure. However, more analysis was needed to ensure this was the case.

If the small growths on the anthraquinone crystals were BHT used as a stabilizer, they would be readily dissolved again in the THF. To test this, a sample was prepared using the stock THF, and was then rinsed with dry THF to see if the flowery growths dissolved. When the two halves were compared, the difference was clear, as seen in Figure 2.21. The unrinsed sample was covered throughout with hairy and flowery growths, while the sample that was rinsed had only straight anthraquinone crystals. Some of the anthraquinone crystals in the rinsed sample were much smaller than in the unrinsed sample, showing that not only were the small extraneous growths dissolved by the stock THF, but the anthraquinone was redissolved to some degree as well, although not as quickly or thoroughly as the extra formations.

As a final test to prove the extraneous formations were BHT, three samples were prepared using 1,4-anthraquinone, dry THF, and BHT. If these samples looked similar to the ones prepared with stock THF, this would show that the extraneous growths were unequivocally formed by the BHT stabilizer in the solution.

All three samples, TH-70-01, TH-70-02, and TH-70-03, were covered with the same formations as the samples made using stock THF (Figure 2.22, Figure 2.23, Figure 2.24). In fact, due to the larger ratio of BHT, the formations were even more prevalent, almost covering the crystals completely in some cases. This positive result once again supports the hypothesis that

the BHT forms smaller formations on the anthraquinone crystals, using the crystals as a substrate for their growth.

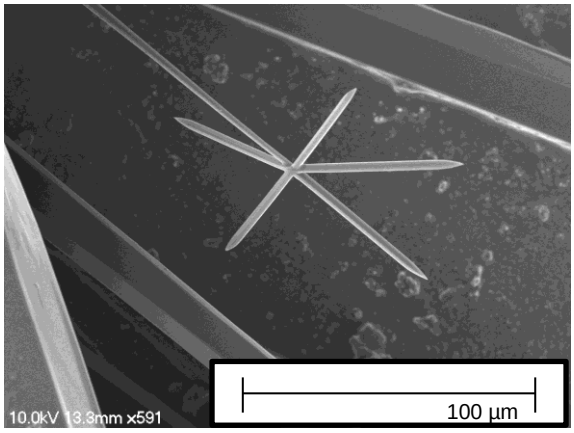


Figure 2.18: Anthraquinone crystals created using dried THF examined under SEM. The needle shaped crystals here are clean and free of any extra growths.

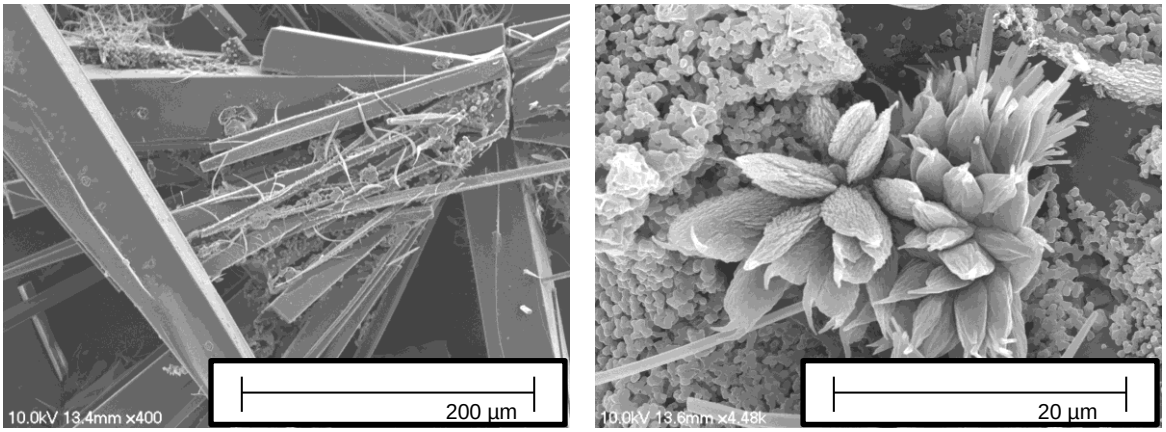


Figure 2.19: Extraneous formations found on anthraquinone crystals created using stock THF, which includes BHT.

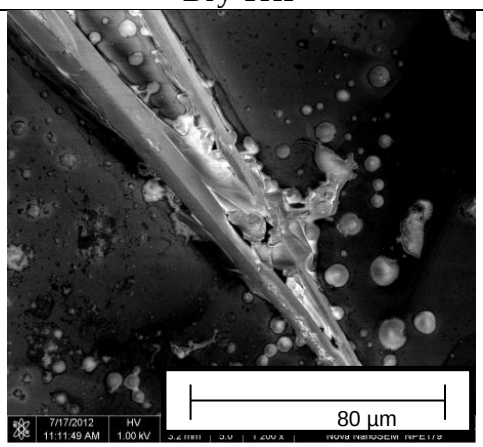
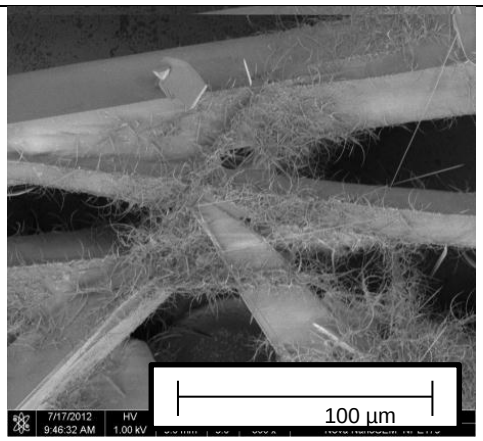
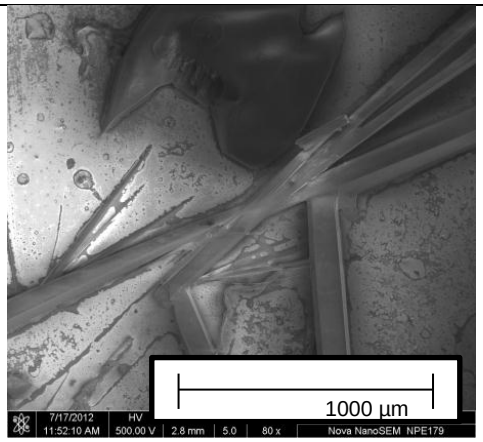
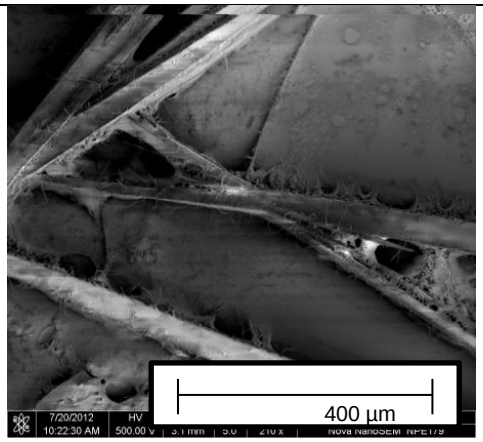
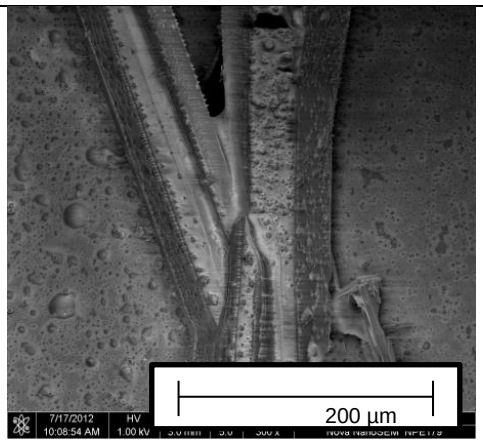
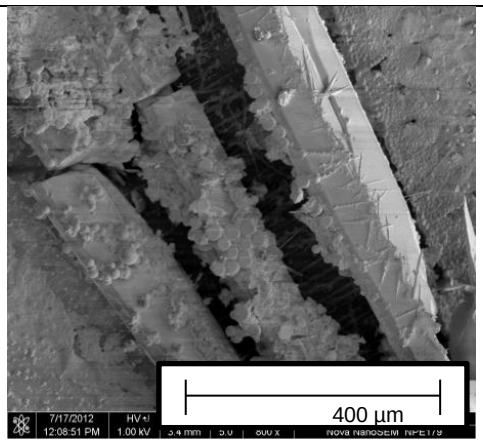
Dry THF	Stock THF
 1% Water	 1% Water
 2% Water	 2% Water
 10% Water	 10% Water

Figure 2.20: Comparison of samples prepared using dry THF and stock THF. Dry THF on the left shows no extra growths, stock THF on the right shows many extraneous growths.

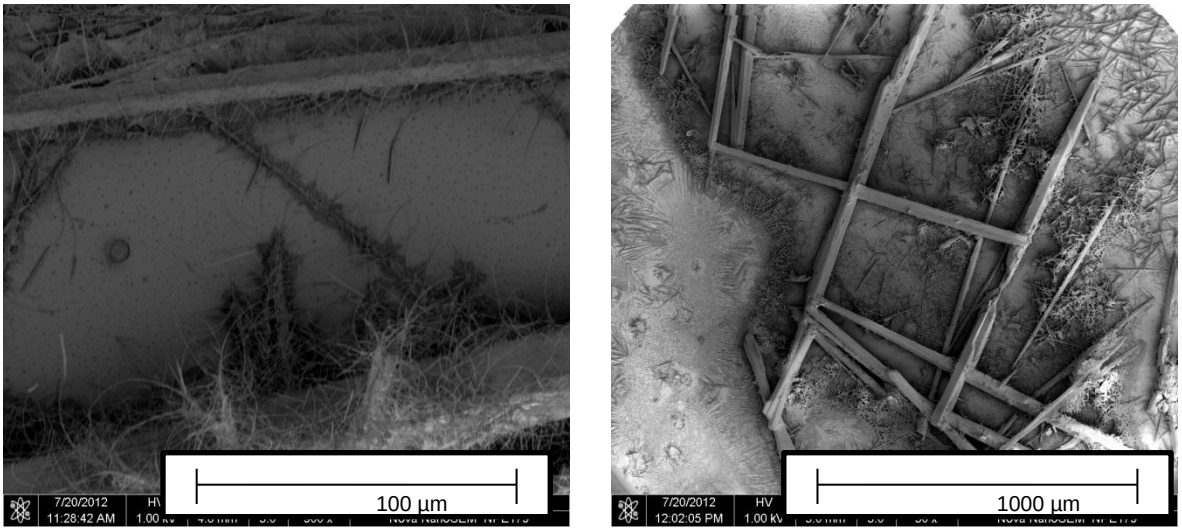


Figure 2.21:. The picture on the left is the sample unrinsed, covered in hair-like growths. After rinsing, on the right, the crystals are clean, demonstrating that the extra growths are soluble in THF.

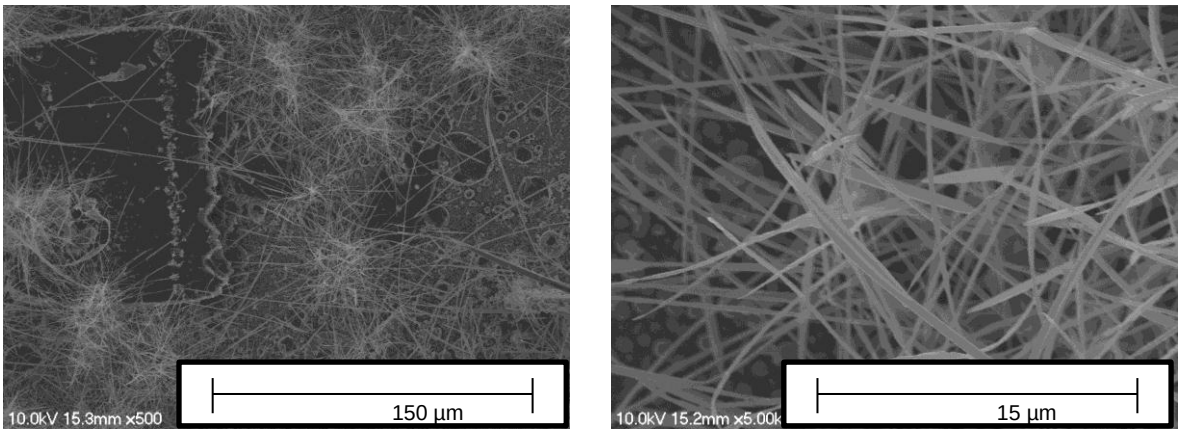


Figure 2.22: Sample prepared with dry THF, 1,4-anthraquinone, and added BHT, covered with extraneous growths

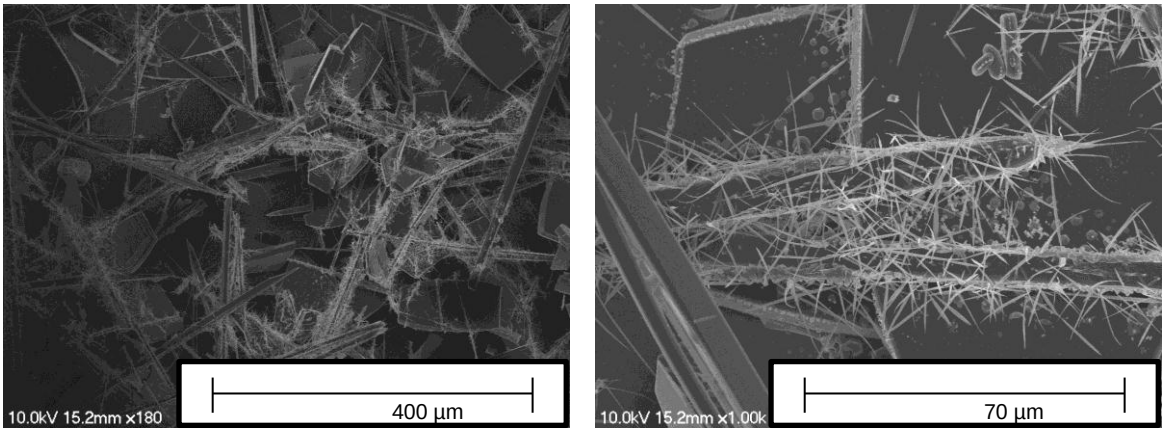


Figure 2.23: Another sample prepared with dry THF and added BHT. The anthraquinone crystals are covered in growths of BHT.

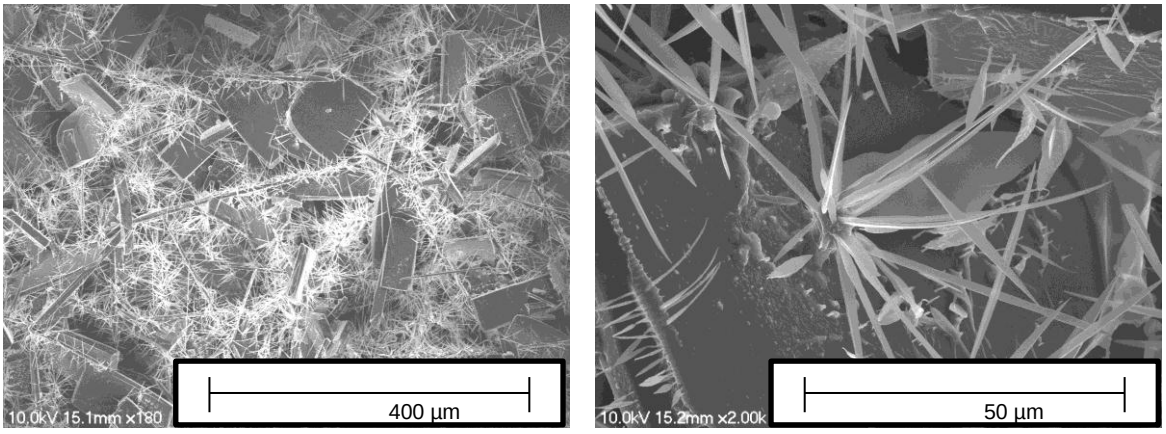


Figure 2.24: A third sample prepared with dry THF and BHT. Again, the extra growths seen previously are highly concentrated throughout the sample.

2.4 Conclusions

Interaction with Water

In general, water tends to disrupt the formation of crystals as the solvent evaporates. In the first sample, with no water present, long, uniform, needle-like crystals of anthraquinone formed over the entire substrate, showing anthraquinone's natural tendency to form ordered structures. The succeeding samples, however, show that these structures begin to break down as water is added to the solution. Sample TH-55-02, with 2% water, still had long needles of anthraquinone, but they were less prevalent and were surrounded by less ordered crystalline deposits. In sample TH-55-03, 10% water, many crystals formed, but they were not nearly as long as in TH-55-01, and their deposition seemed more chaotic than the orderly crystal formed without moisture interference. The trend continued even more sharply with TH-55-04, at 20% water, with only a few long crystals forming. The rest of the anthraquinone was deposited as a grainy film and never formed any sort of crystal at all. Finally, with 50% water, TH-55-05 formed no crystals at all. The evaporation of the solvent left a film of anthraquinone grains on the substrate with no higher order formations visible.

This phenomenon of crystal disruption under the presence of water can be explained by the variance of solubility of anthraquinone in water and tetrahydrofuran. Anthraquinone is insoluble in water, but dissolves well in THF. Water is miscible in THF, so when the two liquids are combined, there is a homogenous solution of liquids. However, the anthraquinone remains only in the THF, and does not dissolve into the water. This mixture of water into the solution causes a separation of anthraquinone particles from one another, which impedes the formation of large crystals, as the anthraquinone molecules cannot build upon one another. Additionally, the THF evaporates much faster than the water. As the THF evaporates, the anthraquinone particles

present in the solution begin to combine into crystals. If large, concentrated amounts of anthraquinone exist, large uniform crystals can form. If the quinone is separated, as by water in the solution, small crystals will form which are then suspended in the water as the THF evaporates. These smaller crystals are then deposited on one another as separate solids, rather than forming larger and larger crystals, as happens with anthraquinone in pure THF.

This behavior is important to take into account when forming quinone crystals, as water has a great effect on the final product. If pure crystals are the goal, care must be taken to keep water from the solution. However, if crystals are not desired, water can be added to the solution to allow anthraquinone to be deposited without forming crystals.

Temperature Dependence

After observing the crystals more closely, it is clear that the plates were indeed formed from 1,4-anthraquinone. Multiple observations support this conclusion. To begin, if the plates had formed from another element besides anthraquinone, it would have been an impurity present in either the anthraquinone or the THF. The anthraquinone used was labeled as pure, while the THF had 250 ppm of BHT, which acts as a stabilizer. There were not enough possible impurities in the solution to account for the large number of plates that formed. Also, the original hypothesis was that the anthraquinone and unknown element formed solids at different times. If that were the case, the plates and needles would have been separated, or the number of needles would have at least decreased on the wafers as the amount of plates increased. This was not the case either, as wafer 2 had the least amount of needles present, and all four wafers had both plates and needles present. Additionally, there were multiple instances found of hybrid crystals, where needles and plates formed in congruence with one another, with needles growing into plates, and needles extending out of formed plates as well. These observances were all cemented

by the NMR results, which shows that the plates share the same resonance spectrum as 1,4-anthraquinone.

Not only did sample TH-67-02 provide conclusive evidence that the plates formed from anthraquinone, it also gave a possible explanation of how the plates form. As the level of the solution dropped due to the evaporation of the THF, the solution began to boil slightly. When the level was low enough to deposit crystals, at a depth of almost the thickness of the silicon wafer, the boiling of the remaining liquid caused bubbles of solution to grow and burst in succession on top of the substrate. As each bubble burst, a thin layer of crystal was deposited. The crystals deposited in these layers were the flat plates observed on the sample, as well as on TH-58-04. This bubbling seems to be the most probable manner of formation; as the bubble pops, the film loses any remaining solvent and forms a solid, flat crystal, similar to that of a frozen soap bubble breaking into flat plates. In fact, similar results have been discussed involving flat-plate ice crystals. It was found that as the thickness of an ice crystal decreased, its condensation coefficient increased, which leads to faster crystal kinetics.[29] Additionally, it has also been shown that as the speed of crystal formation increases, the likelihood of forming sharper edges, and eventually plates, increases as well.[30] This phenomenon explains how the flat crystals of anthraquinone could form in the short amount of time between the bubble popping and the crystals landing on the plate.

This final observation shows that the type of crystal formed can be controlled by physical means, as opposed to chemical means as was predicted. Flat plates can be formed by heating the solution in order to cause bubbles around the susbtrate, where more needles can be formed by allowing the solution to evaporate at standard temperature, without any agitation.

Interaction with Impurities

It has been shown that the extraneous hair-like and flowery growths found on the anthraquinone crystals are composed of BHT. The formations were present in all of the solutions made using stock THF, which contains BHT, they were easily rinsed away with THF, showing that they easily dissolve in the solution, and their presence was seen in the samples made with dry THF and added BHT, confirming their composition as BHT. The coral-like crystals formed by the BHT were surprising due to the compounds molecular shape, shown in Figure 2.25. The unexpected results regarding the BHT are most likely due to the phenomenon of crystal polymorphism, where different crystal structures can form out of the same molecule.[31] This is highly possible in the case of BHT, as polymorphic structures can be formed through hydrogen bonding, and BHT has many options for hydrogen bonding.[31,32] Additionally, flexible molecules are more likely to form polymorphs, and BHT has plenty of branches to create this flexibility.[31]

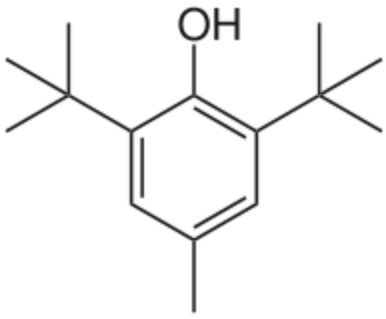


Figure 2.25: Molecular structure of BHT

This observation is important, as it shows that anthraquinone crystals can be used as a substrate for the growth of organic material, which can subsequently be easily removed. This property could be useful in the medical field as a delivery vehicle or in materials studies as a base for organic coatings.

Chapter 3 Summary and Future Work

3.1 Summary

Quinones are a very widely used and widely available compound. They are common in medicine, chemistry, and even the natural world. Though they have been studied extensively for medicine in the form of cancer therapy or pain medication, they are not as well understood in the field of materials engineering. This emerging body of study will encompass many different forms of quinone, including 1,4-anthraquinone. 1,4-anthraquinone is a simple molecule which is readily available and easy to study, and it has already shown promise in materials engineering, specifically when used in the creation of metal organic frameworks. In order to better understand 1,4-anthraquinone and its possible uses, its structure and properties need to be understood, as well as what determines the types of formations which can be created. As a starting point, this thesis observes the formation of 1,4-anthraquinone crystals when subjected to various amounts of water, elevated temperature, and the addition of other minor elements.

Interaction with Water

The effects of water on crystal formation of 1,4-anthraquinone were analyzed by comparing solutions with varying amounts of added water. Five solutions were made in all, using 1,4-anthraquinone, tetrahydrofuran, and one each with 0%, 2%, 10%, 20% and 50% water by volume. After allowing crystals to form, it was observed that the water tended to impede the larger, uniform crystals generally seen with anthraquinone. With no water added to the solution, long uniform needles of anthraquinone formed on the substrate. At 2% water, long needles still formed, but some of the anthraquinone was deposited as a sort of film, rather than forming into crystals. At 10% water, the crystals that formed were much smaller and more chaotic than

regular anthraquinone crystals, with small needles growing in every direction from a center point. 20% water inhibited much of the crystal growth, rendering only a few needles with mostly grainy deposits of anthraquinone on the substrate. 50% water in the solution did not allow any crystals at all to grow, leaving only layers of deposited anthraquinone on the substrate.

The crystal growth inhibition caused by added water is due to the fact that 1,4-anthraquinone does not dissolve in water as it does in THF. When the THF mixes with the water, it distributes itself and the anthraquinone evenly throughout the solution. With more added water, the anthraquinone will be separated more, and thus will not be able to form as many large, ordered, crystals. This observation shows the importance of maintaining a moisture free environment if many crystals are to be obtained. Conversely, if the goal is to deposit anthraquinone with creating crystals, water can be added to the solution to achieve this end.

Temperature Dependent Kinetic Formation

At standard temperature and pressure conditions, the preferred type of crystal formation for 1,4-anthraquinone is in the form of needles, with a few small plates present on the substrate. It was found, however, that when the solution was heated, plates formed much more readily. Initial observations seemed to indicate that these plates were formed of another compound besides anthraquinone. To understand what caused the plates to form, and what the plates were made of, crystal formation was observed while the solution was heated.

As the solution evaporated and deposited a layer of crystals on the substrate, the substrate was removed and replaced with a new one, in an effort to separate the plates from any initial needles that may have formed. This was repeated until four samples were obtained. The four samples were observed under an optical microscope and compared to one another, and one of the

samples containing the least amount of needles with the greatest concentration of plates was chosen to undergo nuclear magnetic resonance scanning. The NMR results indicated that the plates were indeed composed of 1,4-anthraquinone, as they matched previous NMR results of the compound. Additionally, hybrid crystals were observed on the samples, with plates and needles connected and growing together. It is unlikely these hybrids would form if the crystals were two different elements. Also, the concentration of plates found on the sample far outnumbers any sort of additive the solution may have contained, leading to the conclusion that the plates could only have formed from 1,4-anthraquinone.

The plates most likely were caused by boiling in the heated solution as the solvent level dropped below the substrate. As the solution boiled, the bubbles grew over the substrate, forming a film of solution saturated with anthraquinone. When the bubbles popped, this film of anthraquinone could solidify as the solvent evaporated, allowing newly formed plates to deposit. With these observations, it can be concluded that 1,4-anthraquinone can form different crystals depending on the physical surroundings, even with the same chemistry present. In this case, higher temperatures created instances of flat plates forming due to agitation. Future researchers can use this observation to control the shapes formed by anthraquinone crystals, choosing plates when a flat crystal is needed or needles when a longer, skinnier crystal is necessary.

Interaction with Impurities

Upon general observation of many of the anthraquinone crystals, it was noticed that some samples contained extraneous formations that occurred on top of the anthraquinone crystals. These growths looked like small hairs or coral, and seemed almost organic in nature. A pattern emerged in that these formations seemed to appear on samples made with regular tetrahydrofuran, which includes butylated hydroxytoluene as a stabilizer, but were absent on

samples formed with dried THF as the solvent. This led to the hypothesis that impurities in the solution, such as BHT, were forming the new shapes after the anthraquinone crystals provided a substrate. In order to confirm this hypothesis, a series of experiments were conducted.

The first analyzed six samples, three of which were made using the stock THF, and three of which were made using dry THF. The three samples for each type of THF also had varied amounts of deionized water, to ensure moisture in the solution wasn't causing any strange shapes to form. After observation, it was clear that the samples made using dry THF were composed of only anthraquinone crystals, while the samples made with the stock THF did indeed have these extra formations.

The second experiment to test the formations on the anthraquinone was to compare two pieces of the same sample when subjected to different conditions. A sample was prepared using stock THF, and once the crystals were deposited, the substrate was broken into two parts. One half was kept for observation, while the other half was rinsed quickly in dry THF. The unrinsed half contained many of the small hairs, while the rinsed half had only clean anthraquinone crystals. This gave further support to the hypothesis that BHT was forming the new growths, as it would be dissolved by THF upon contact. Additionally, this also showed that the smaller formations dissolved into solution before the anthraquinone crystals, and the anthraquinone crystals could be cleaned if necessary.

The final experiment was to make a solution comprising of 1,4-anthraquinone, dry THF, and added BHT. Three samples were created, and each sample showed the same formations as the samples made using stock THF. This final observation can be used to conclude that the small, hairy formations were indeed BHT. This conclusion is important, as it shows that anthraquinone

crystals can be used a substrate for layers of organic material. Anthraquinone crystals could be used a vehicle for organic materials, such as transporting medicine, or they could be used as a substrate for coating of organic material.

Concluding Remarks

The wide use and availability of quinones make them an important topic to study, as they have effects on chemistry, medicine, and engineering. Quinones are just beginning to be explored in a materials engineering perspective, and show some promising results. 1,4-anthraquinone specifically is a good candidate for research as it is widely available, a simple molecule, and is not yet in high demand for any purpose. Understanding the structure of 1,4-anthraquinone, as well as how to manipulate that structure, is important going forward in order to make 1,4-anthraquinone a useful component. As demonstrated by this thesis, 1,4-anthraquinone crystals can be manipulated with the addition of water to the solution, agitating the solution by heating, and introducing other compounds to the solution that interact with the anthraquinone crystals. These forms of manipulation only begin to show what can be done using quinones, and should be researched further, in an effort to continue to expand the knowledge of quinones as they relate to materials engineering.

3.2 Future Work

The studies described in this thesis are simply a beginning on the studies of 1,4-anthraquinone, and provide a useful platform for continual research. Each area is deserving of more study, especially in the focus described below.

Interaction with Water

Anthraquinone's interaction with water is deserving of further study, as it allows for a simple mechanism to control whether or not large ordered crystals form. Particular effort could be applied to the situation of 10% water by volume, as the results for this sample were particularly interesting. The highly chaotic and interlocked layer of quinone crystals could be useful in applications, and the physical interactions between the crystals should be reviewed.

Additionally, the coffee ring deposits found in the samples being tested for interactions with impurities seem to be caused by added water in the solution. This would be another interesting avenue to study, as this is a relatively new area of study, and prospects for the self-assembled rings seem to be very high. [28]

Temperature Dependence

It would be interesting to determine if plates can be formed by other methods rather than just heating the solution and allowing it to boil, especially if this were undertaken on a large scale. Heating a large amount of solution would become energy inefficient. It might be possible to form plates by bubbling gas through the solution, and using those bubbles in the same way as the bubbles created by the boiling solution. This approach would need to be tested to determine if it is only the bubbles causing the plates to form, or a combination of bubbles and higher temperatures.

Another avenue of study to consider regarding temperature would be to study the effects a different range of temperatures has on the crystal formation. Only one temperature was analyzed in this study, and it is possible that other temperatures could create different types or variations of other crystals.

Interactions with Impurities

The interaction between anthraquinone and organic compounds such as BHT is of great interest. This study has shown that 1,4-anthraquinone can serve as a suitable substrate for BHT, and this knowledge can be applied to other organic compounds. Future research should focus on how anthraquinone interacts with other organic compounds, and could easily begin to explore uses in this area. It would also be interesting to compare the growth of BHT on anthraquinone to its growth on other surfaces, to see if BHT is affected by the anthraquinone, and to see if other BHT polymorphs can be formed.

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