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Article

Crystallization kinetics of vanillin thin films

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SUMMARY

Due to its anisotropic crystal structure, vanillin exhibits unique optical interference when interacting with light. We chose vanillin as an exemplary material system to study the relationship among its microstructure, growth behavior and optical characteristics. In this study, we grew vanillin thin films on microscope glass slides and observed the emergence of tiny crystallites and their continuous growth until these crystals impinged upon each other and fully covered the entire glass slides. Intrigued by the underlying driving force to transform vanillin liquids into translucent crystalline films, we started to investigate their nucleation and growth mechanism. We hypothesized that these crystal thin films behave differently depending on the type of crystallization method. We studied the nucleation density and growth rate of vanillin crystallization from three different methods: from a melt, from a solution, and from a solution but on a silane coated glass surface. The difference in nucleus formation among these three conditions can be qualitatively understood by the thermodynamic free energy theory, where undercooling is the main reason for crystallization from a vanillin melt, and supersaturation and diffusion are responsible for vanillin crystallization from a solution. We also quantitatively studied the growth rates of these vanillin films using the classical Avrami theory. The crystal grain size ratio measured experimentally correlates relatively well with the prediction from the Avrami Equation. In conclusion, this work provides a deeper understanding of thermodynamic and kinetic aspects of thin crystalline film nucleation and growth, which may shed further light on fundamental parameters to engineer thin films through a self-assembly process for certain applications, such as micro or nanoscale optical devices.

INTRODUCTION

Crystallization is the process of arranging disorderly molecules into highly organized crystal structures. Once crystallized, some materials exhibit unique electrical and/or optical behaviors. For example, distinctive optical fringes can occur with anisotropic crystals (1). One common way to grow crystals is through precipitation from a liquid. This process is essentially a phase transformation. The fundamental driving force behind changing the state of a substance from liquid to solid is a drop in the overall system's thermodynamic free energy. When the change in the system's Gibbs free energy becomes negative, the solidification process becomes thermodynamically feasible (2). However, to create a nucleus, the initial tiny cluster of crystal matter, an "uphill" activation barrier needs to be overcome (2). This activation energy is called the critical free energy and is necessary to create a nucleus size that is stable to prevent dissolution back to its liquid state. After a stable nucleus forms, crystal growth occurs (2). This classical crystal nucleation and growth theory applies to a variety of materials, including ceramics, metals, and polymers (2).

Crystals are usually precipitated from melted pre-existing crystals or from solutions (3). In the case of melting, the material is liquified by being heated above its melting temperature; then it is cooled down to allow solidification into its crystal form. In solution crystallization, the material is first dissolved in a solvent and then precipitated into its solid form when the solvent evaporates. Crystallization is often used to grow a high purity, structurally ordered crystal phase out of its original form, for example, a structurally disordered powder.

For crystallization in the case of melting to occur, there may be one or multiple controlling processes such as mass transport, heat flux, or a chemical reaction across a solid-melt interface (4). The dominating crystallization mechanism depends on the degree of undercooling and the magnitude of latent heat of the specific material during liquid to solid phase conversion (4).

In the case of crystallization from a solution, LaMer described three stages for crystal films growth mechanism (3,5). At stage one, nucleation occurs when the solution reaches a supersaturated state. In stage two, the nucleation continues with the supply of molecules to the nuclei through diffusion. When the solute's rate of consumption is faster than the available supply (for example, by solvent evaporation), nucleation stops. In stage three, only the growth of the nuclei continues. Overall, the competing processes of nucleation and growth determine the final crystal grain size and grain counts. Furthermore, Von Weimarn's theory provides an empirical equation to describe the exponential relationship between the nucleation rate and the level of supersaturation in a liquid state (5). Within the framework of diffusion-controlled crystallization processes, Fick's Laws of Diffusion describe the transport of solutes from the solution to the crystal interface, contributing to the growth of existing crystals (3). According to Fick's Laws, the concentration gradient between the bulk solution far away from the nucleus and the solution immediately around the nucleus drives the movement of molecules into a growing crystal.

Vanillin (4-hydroxy-3-methoxybenzaldehyde) is commonly

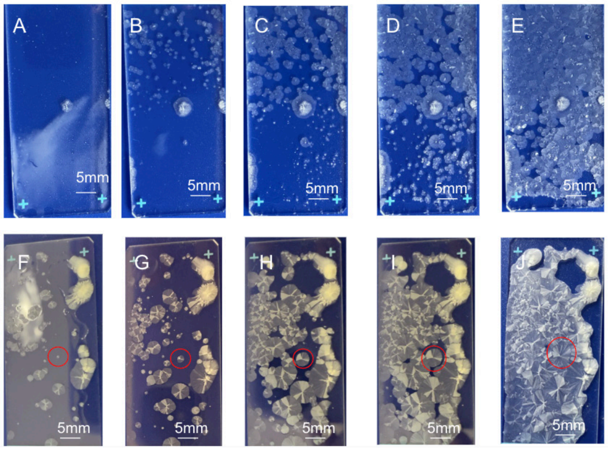
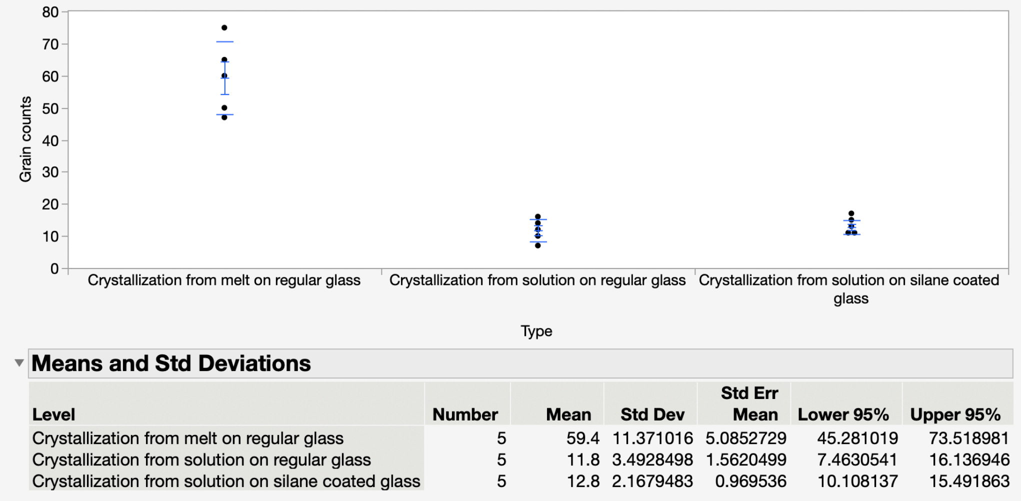


Figure 1: Representative images of nucleation and growth of vanillin grains on glass microscope slides over time for recrystallization from melt and solution. Formation of vanillin film from a melt on a microscope glass slide after A (5 seconds), B (10 seconds), C (15 seconds), D (20 seconds) and E (25 seconds). Formation of vanillin thin film from solution on a glass microscope slide after F (25 seconds), G (50 seconds), H (75 seconds), I (100 seconds) and J (125 seconds) happened sequentially. Red circles track a single vanillin grain from its initial appearance with diameter less than 0.5mm (F) to its growing to around 5 mm in diameter (J). The growth stopped at stage J because neighboring grains impinged upon each other.

used for flavoring or fragrance. Due to its anisotropic crystal structure, the vanillin thin film interacts with light and exhibits unique optical interference. Therefore, we chose the vanillin crystal film to study effects of its microstructure and growth kinetics on its optical characteristics. In our previous study, we learned that vanillin thin films are semi-crystalline with a spherulite type of morphology (6). Here spherulite refers to a well-developed vanillin grain, while nuclei refers to the initially formed clusters of vanillin molecules which can further develop into spherulite grain. A vanillin crystal is a general term referring to its well-ordered molecular structure, including nuclei and spherulite. In this study, we continue to examine the growth behavior of vanillin thin films, aiming to understand the guiding principles for the nucleation and growth of vanillin crystalline films. We selected vanillin for this recrystallization study because we can repeatedly produce translucent thin films with measurable crystal growth rate. This method to recrystallize thin films such as vanillin may provide a low-cost alternative to traditional micro- and nanofabrication processes. For example, one common approach to produce thin films is through a vacuum sputtering process where the material source is bombarded away by high energy argon gas and redeposited on a substrate in a well-controlled thickness (7). This process requires a high precision vacuum chamber typically placed in a clean room facility of class 10 (e.g., class 10 cleanroom allows maximum number of particles with a diameter of 0.5 micrometers per cubic foot space). The cost to establish and maintain such a nanofabrication facility is prohibitive; usually researchers across the country use shared facilities placed in a few universities such as Cornell Nanoscale Science & Technology Center (8). Low-cost fabrication processes using polymer thin films are being studied but are still at the early stage of producing functional nano devices (9).

We hypothesized that the quantity and growth rate of vanillin crystals in thin films depend on the degree of undercooling when crystallizing following melting and supersaturation when crystallizing from a solution. In the case of melt-based solidification, the temperature delta between its liquid state and solid state, also called the degree of undercooling, is the main driving force for its nucleation and growth (2). The larger the degree of undercooling, the faster crystallites form and grow. In the case of solution-based recrystallization, the driving force is the concentration gradient surrounding the crystallites, namely the degree of supersaturation. When crystallites grow and consume vanillin molecules in nearby solution, far-away molecules can travel to near crystallites through diffusion and continue to support crystal growth. Therefore, the higher the concentration gradient, the faster crystallites will grow.

We suspect that vanillin films grown from melted crystals may grow faster than those from solutions. The underlying



Means and Std Deviations

Level	Number	Mean	Std Dev	Std Err Mean	Lower 95%	Upper 95%
Crystallization from melt on regular glass	5	59.4	11.371016	5.0852729	45.281019	73.518981
Crystallization from solution on regular glass	5	11.8	3.4928498	1.5620499	7.4630541	16.136946
Crystallization from solution on silane coated glass	5	12.8	2.1679483	0.969536	10.108137	15.491863

Figure 2: The number of vanillin grains formed from three conditions. The grain counts for each crystallization condition were measured when recrystallization was completed, and vanillin grains covered the entire glass slides. The size of each slide was 75 x 25 mm^2 and grain counts are per slide with five slides for each condition.

reasons are probably two-fold: one is higher thermodynamic driving force, and the other is related to higher vanillin concentration in a melt than in a solution. As our vanillin crystals are formed in a two-dimensional thin film instead of a bulk crystal, we also assumed that the glass surface property might play a role to modulate their growth behavior too.

To test our hypothesis, we designed three vanillin crystallization systems. The first crystallized melted vanillin into a thin film on a glass slide, the second dissolved vanillin in a solution and crystallized it on a glass slide, and the third crystallized vanillin out of a solution onto a silane coated glass slide. Silane coating is a typical surface modifying agent which could possibly change the interfacial adhesion and thus either promote or hinder vanillin film crystallization process. We chose glass substrates so we could observe the film growth behavior using a transmitted light optical microscope. We recorded the process of crystal emergence and propagation and measured the growth rate of the vanillin films. We analyzed our data by leveraging crystallization theories to understand the science behind vanillin crystals' nucleation and growth. We learned that vanillin films grow much faster out of a melt than out of a solution, and they follow different crystallization mechanisms. For crystallization out of a melt, undercooling is the dominant driving force, while that out of a solution, the degree of supersaturation is the key factor.

In the longer term, we hope that this study can help in engineering thin film systems with significant optical applications via self-assembly by crystallization rather than through an expensive fabrication process (7–10). Our approach relies on self-assembly of vanillin molecules into its native crystal structure with the intrinsic driving force being intermolecular bonding of these molecules and thus is independent of sophisticated equipment to process them. This could contribute to applications like building inexpensive micro- or nanoscale optical electronics devices in the future.

RESULTS

We grew vanillin thin films on glass slides and observed the emergence and growth of these crystals. We chose glass substrates so we could observe the film growth behavior using a transmitted light optical microscope. We formed each film using one of three types of methods. The first method was to melt vanillin powder and crystallize it on a glass microscope slide. The second was to place a few droplets of vanillin solution on a glass microscope slide and let the solution crystallize into thin vanillin films. The third condition was the same as the second condition except that the glass microscope slide was pre-treated with silane, a coupling agent that enhances bonding between chemically inert glass and the vanillin droplets on the glass's surface. We captured the crystallization process of these three types of vanillin films over time to understand the progressive steps necessary to nucleate and grow these films. We divided our results into three sessions including crystal growth process observation, crystal growth rate and crystal growth mechanism.

Crystal growth process observation

First, we observed the crystallization of melted vanillin. Initially, spherulite shaped crystals appeared on seemingly random locations on the glass slides while the liquid melt was still visible (**Figure 1A**); after 5 seconds, more spherulites appeared along with the growth of existing spherulites (**Figure 1B**). The existing crystals continued to grow, and few new crystals were formed over the next 5 seconds (**Figure 1C**); Finally, these spherulites almost impinged on each other, leaving very limited space for growth (**Figure 1D**). After about 25 seconds since initially plating the melted vanillin, the crystals reached their final stage where they stopped growing (**Figure 1E**). We then grew vanillin crystals out of a solution. Starting with a few spherulites in the solution, more spherulites emerged and also grew larger until the liquid phase was depleted and crystals stopped growing (**Figure 1F-J**). When crystallizing vanillin out of its solution on a silane modified glass slide, we observed similar film morphology to that of vanillin crystals formed from a solution on an uncoated

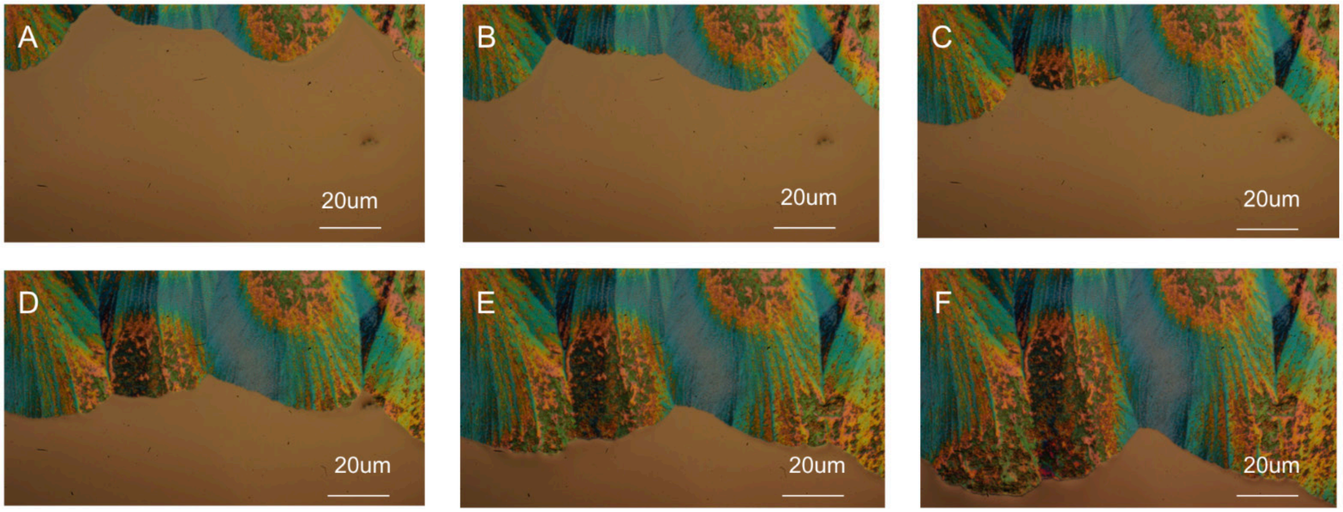


Figure 3: Representative time-lapse images of vanillin film growth captured under a polarizing optical microscope. This series of images show vanillin film crystallization from a solution. The growth front of the film was captured from images A to F. There were 4.5 second intervals between adjacent images.

glass slide**.**

One interesting difference is that vanillin films grown from a melting had more nuclei and smaller final crystal sizes than the film grown from a solution**.** After crystallization was complete, we counted the number of spherulites on each glass slide for a total of five glass slides per condition (**Figure 2**). Each spherulite was treated as one single vanillin grain. The average grain count from the melt was about 61 grains per glass slide, while the grain counts from solutions averaged around 12 grains per glass slide regardless of glass coating. This data shows that vanillin grains formed through the melting process were about five times smaller than those formed from solutions, and that the number of nuclei of melt-created vanillin grains was about five times more than those created from solutions. based on the properties of vanillin, we calculated a first order estimate of the critical nucleus size of our vanillin crystals formed from a melt and found it to be 0.025 µm. Thus, when the vanillin nucleus size is greater than 0.025 µm, it will overcome its nucleation barrier and grow into a spherulite grain instead of re-melting into its liquid form (11). The observable nucleus size in our experiment was about 1 µm, which is the limit of our optical microscope resolution. One µm is well above the threshold value of 0.025 µm, so we cannot verify that 0.025 µm is an accurate critical nucleus size.

Crystal growth rate

We also captured the growth of these vanillin films and measured their growth rates by taking time-lapsed images under a polarizing optical microscope so we can further study the growth kinetics of these films (**Figure 3**). We measured the length of each growth and used the timestamps on the images to convert this length into a growth rate (m per second). These images are colorful because of the optical birefringence patterns generated by a polarizing microscope; the detailed description of color patterns can be found in our prior study (6). We discovered that the film growth followed a linear function for all three conditions, with R-squared values greater than 0.98 (**Figure 4**). The vanillin growth rate from the melting process was about four to five times faster than that of vanillin grown out of a solution (**Figure 4**); this correlates well with the finding that crystallization from a melt formed about five times more vanillin grains than that from the solutions. Additionally, the growth rate of films grown on silane coated glass is about 68% compared to that grown on regular glass.

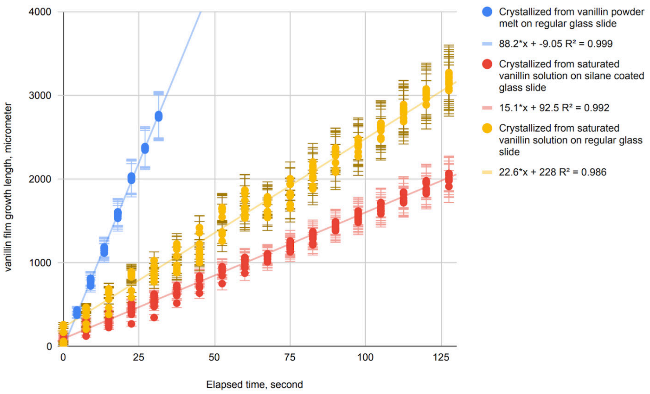


Figure 4: Vanillin film growth length as a function of elapsed time. Data were collected on three film growth conditions, one is crystallization from a melt (blue color), second is from a solution on silane coated glass (yellow color), and third is from a solution on regular glass (red color). Total 10 data points were taken at each time stamp. Error bars represent percent error for each data point by comparing with predicted true value.

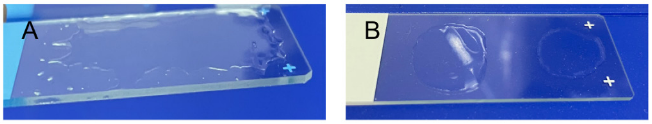


Figure 5: Wettability of silane coated (A) and regular (B) glass slides. Two individual drops of 91% isopropyl alcohol were placed on each slide with the droplet volume of 0.5 mL measured by a medicine dropper. The extent of spreading is an indication on the wetting behavior of these droplets, where more spreading indicates better wetting.

The driving force for crystal films grown from solutions is the degree of supersaturation (10–12). Supersaturation refers to the concentration of vanillin molecules in the solvent exceeding the solubility limit without precipitation (10–12). In our study, a first order estimate of the vanillin crystal growth velocity in the case of solution with a diffusion-controlled process gives a value of up to 53 µm per second, assuming a *D,* diffusivity, of 1600 m^2/s; nucleus radius, *r*, of 0.025 µm; ρ of 1060 kg/m^3; and volume fraction, f, of 0.8 (13–15). The detailed description on calculating the crystal growth rate can be found in the Materials and Methods session. Our experimental data shows about 15 to 22 µm per second growth rates (**Figure 4)**. Though not exactly the same, the crystal growth rates measured from our experiments and calculated from Fick's Law based diffusion model are in the same order of magnitude.

In order to further elucidate the relationship between the growth rate of crystallized vanillin films and the surface treated glass slides, we did a surface wettability experiment by comparing the degree of spreading of vanillin solution on both silane-coated and regular glass slides. In a surface wettability test, the level of spreading is determined by the balance of cohesive force within the liquid and adhesive force between the liquid drop and the glass substrate. A larger spreading indicates stronger adhesion between vanillin and the glass surface (13). When we deposited our solvent droplets onto the silane coated glass, they quickly spread out and formed a thin layer on the glass (**Figure 5A**). On the other hand, when we placed droplets onto a regular glass slide, they only spread moderately (**Figure 5B**). By rough estimate, the spreading areas of droplets on silane coated glass slides was about two times more than on regular glass slides.

Crystal growth mechanism

We also explored and interpreted our film growth rate data using the Avrami equation. The Avrami equation describes the kinetics of phase transformation, such as crystallization (17–19). The speed of phase transformation often follows an *s*-shaped curve, where the rate is slow at both the beginning and finishing stages but rapid for the main stage of the transformation. The slow rate at the beginning stage is related to the nucleation incubation time, and the final slow rate is due to limited remaining matter available for further

Categories	**Case 1: crystallized from melt on regular glass**	**Case 2: crystallized from solution on regular glass**	**Case 3: crystallized from solution on silane coated glass**
Averaged number of grains	59.40	11.90	12.80
Averaged grain size (mm)	3.17	7.08	6.83
Ratio of grain size by measurement	0.46	1.04	1.00
Grain growth velocity μm/second	88.20	22.60	15.10
Nucleation time, second	0.20	1.52	2.00
Nucleation rate, counts/second	297.00	7.93	6.40
Ratio of grain size by calculation	0.50	1.06	1.00

Table 1: Comparison of vanillin grain size ratios from the experimental measurement and our theoretical calculation based on the Avrami equation among three crystallization conditions. Grain size ratios were normalized by values of case 3.

nucleation and growth. During the intermediate period, the nuclei grow into solids and consume adjacent liquid phases, resulting in a rapid transformation from liquid to solid.

Assuming random nucleation and identical growth rate in all directions, Avrami derived the equation of the crystal growth rate with respect to time (17–19). The equation dictates that the final grain size is dependent on the one third power of the ratio of the growth rate to the nucleation rate for two-dimensional constrained crystal growth conditions, such as thin film geometry in our study.

We applied a semi-quantitative analysis using the Avrami equation to predict the grain size of vanillin crystals formed under the three conditions in this study and compared the predicted size with the experimental data we collected (**Table 1**). This analysis confirms that our vanillin crystal growth follows Avrami kinetic behavior for both solution and melt based crystallization process; however, we cannot correlate the absolute growth rates well yet.

DISCUSSION

In this study, we studied vanillin film's crystallization out of its solution and or melt and collected data to describe its growth behavior at three different conditions, with two out of solutions and one out of a melt. Our experimental data shows that crystallization of vanillin from a melt yields about five times more crystal grains and grows about four to five times faster than the same crystallization from a vanillin solution. These two solidification processes are fundamentally different in terms of the driving forces behind nucleation and growth: one is driven by degree of undercooling for the melted crystals and the other by the level of supersaturation of the solution (11).

We have observed that the growth rate of vanillin films on silane coated glass is about 68% of that on regular glass. Our solution spreading experiment showed that the vanillin solution spreads to a larger extent on a silane coated glass than on a regular glass. Silane is a surface coupling agent, which chemically bonds with inorganic substrates (in our case, glass) on one end and with organic molecules (in our case, vanillin) on the other end (17). This leads to enhanced adhesion between vanillin droplets and glass surface and likely is the reason for the increased spreading we observed on silane-coated glass (20). The bonding between the vanillin solution droplets with a regular (non-coated) glass surface is a typical weak hydrogen bond, which explains the poorer wetting and spreading (20). We illustrated the interfacial bonding characteristic by comparing these two cases (**Figure 6**).

Based on what we learned about the role of silane surface modification, we hypothesize that the enhanced chemical bonding between the vanillin solution and silane coated glass slows down the mass transportation of vanillin molecules to the already formed nucleus and therefore limits diffusion-assisted vanillin crystallization (20). In the case of regular glass, less wetting means more available vanillin molecules in the solution next to the nucleus. These vanillin molecules do not bond strongly with a glass surface and therefore have higher mobility, leading to a higher ability to contribute to crystal growth. This helps explain why the vanillin crystallization growth rate is slower for silane coated glass slides than for regular glass slides.

In this study we also observed that vanillin crystals grow faster out of a melt than from a solution. In general, literature on crystal nucleation and growth notes that crystallization from melting is much faster than that from a solution (21). It is possible that the driving force provided through undercooling is much higher than that through supersaturation. To further validate this model in the future, we would need to rely on advanced characterization tools such as differential scanning calorimetry to track the percentage of crystal conversion from a liquid form and develop an empirical scaling factor for our vanillin system.

Additionally, for our experiment of vanillin film crystallization out of a melt, we cannot control the ambient temperature in our home lab setup. Similarly, we could not accurately measure vanillin concentration in solution with the home lab setup.

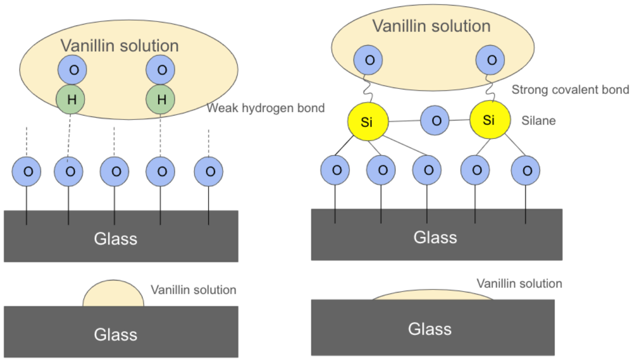


Figure 6: Interactions of silane coated glass and regular glass with a vanillin solution. Left: weak hydrogen bonds between vanillin molecules and regular glass lead to less spreading of vanillin solution. Right: strong covalent bonds between vanillin molecules and silane-coated glass through silane coupling agent enhances spreading of vanillin solution.

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Rather, our goal was to compare the nucleation and growth mechanism of two different setups. Access to advanced materials synthesis and characterization tools such as an environment chamber to better control temperature during the crystallization process and a scanning electron microscope to verify vanillin phase compositions, will help to clarify a few outstanding questions in this work. In the longer term, we will further explore the fabrication of optically significant structures and devices using the crystallization process developed in this study. If successful, this would enable a lower cost micro-scale fabrication process compared to the conventional approach, which relies on expensive fabrication equipment and processes.

MATERIALS AND METHODS

99% high purity vanillin, $C_8H_8O_3$ (CAS number: 121-33-5, ChemCenter), was used in this study. The substrates to grow thin film vanillin were microscope glass slides (AmScope). Uncoated and silane coated slides were used. Three types of vanillin crystallization experiments were performed: melting vanillin powder on regular microscope glass slides and letting crystals grow, depositing vanillin solution on regular glass slides and waiting for crystallization and depositing the same vanillin solution on silane coated glass slides and waiting for crystallization. We prepared 5 samples for each condition for a total of 15 samples for all 3 conditions in order to account for sample-to-sample variations.

We prepared vanillin solutions by continuously adding vanillin powder into a mixture of 91% isopropyl alcohol and water until tiny vanillin particles became noticeable. We deemed this state as the saturated vanillin solution. The saturated concentration of vanillin was roughly 10 mg/mL. We prepared these solutions at room temperature. We selected a mixture of isopropyl alcohol and water as the solvent in order to produce stable vanillin crystal films (7). For each experiment, 0.5 mL vanillin solution was placed on the glass slide.

To melt vanillin samples, we placed around 1 gram vanillin powder on the microscope glass slide, then placed the glass slide on a hot plate and heated until vanillin visibly melted. Then we removed the glass slide from the hot plate and observed the growth behavior of vanillin crystals at room temperature.

Afterwards, we observed and recorded the nucleation and growth of vanillin crystal films under a transmitted light microscope, namely Olympus BH-2. This BH-2 microscope is capable of taking polarizing images using the attached polarizer, analyzer, and retardation plate. A 16-megapixel digital camera was attached to the microscope to take images at varying magnifications. We recorded the crystallization of our vanillin films over time and measured the growth length through a measurement feature in Adobe Photoshop. For each film's growth front, we took ten measurements to account for a lack of uniformity in the growth front. We then compiled the measurement data into Google Sheets and plotted out all vanillin film growth lengths as a function of the elapsed time. Afterwards, we analyzed the plots by curve fitting using linear regression.

We also prepared five samples of each condition at 1X magnification to capture the emergence and growth of vanillin crystals across the entire microscope glass slides and counted the total vanillin grains after crystal growth stopped. Each spherulite was treated as one single vanillin grain. We then averaged the number of grains per condition by dividing grain counts by the covered glass slide's total surface area (75 x 25 mm^2).

For solvent wettability testing, we placed two individual 0.5 mL vanillin solutions on each slide. We calculated the critical nucleus radius using Equation 1

$$r_c = \frac{2\gamma T_{melt}}{q_s \rho \Delta T} \qquad \text{[Equation 1]}$$

where ΔT refers to the difference between ambient temperature and melt temperature, $T_{ambient}$ refers to the crystallization temperature (25°C in our experiment), and T_{melt} is 81°C for vanillin (11). Therefore, approximately 56°C of ΔT exists to help vanillin crystallize out of its melted form. We can obtain a first order estimate of our vanillin crystallization from a melt is 0.025 µm given that undercooling ΔT is 56°C, vanillin liquid surface tension γ is 0.0473 N/m, density ρ is 1060 kg/m^3, and solidification heat qs is 22400 J/mol and T_{melt} of 81°C (11).

Assuming vanillin crystal starts with a spherical nucleus, with radius r, the growth velocity for a diffusion controlled solid/liquid system can be described by Equation 2

$$\frac{\partial r}{\partial t} = \frac{DC_0}{rf\rho} \qquad \text{[Equation 2]}$$

where *D* is the diffusion coefficient, C_0 is the initial concentration, *r* is radius of a spherical nucleus, and ρ is density, and f is the volume fraction of solid crystal in liquid (15).

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