Supporting Information for

"Crystal Engineering of L-Alanine in the Presence of L-Leucine Additive using Metal-Assisted and Microwave-Accelerated Evaporative Crystallization"

Adeolu Mojibola, Gilles Dongmo-Momo, Muzaffer Mohammed and Kadir Aslan*

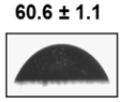
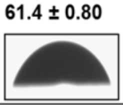
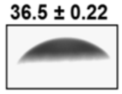
Morgan State University, Department of Chemistry, 1700 East Cold Spring Lane, Baltimore, MD 21251 USA

* Corresponding author: Kadir.Aslan@morgan.edu

1. Characterization of SNFs

To determine the extent of surface modification of silver nanostructures (SNFs) on PMMA, the contact angle and surface tension of water and L-alanine solution on PMMA and SNFs-PMMA were measured using the drop shape analysis method. The results obtained from these parameters are shown in (Supporting Information, Table S1); the contact angle of L-alanine solution on blank PMMA was 62.1°, and on SNFs-PMMA was 60.6° after obtaining the average of 3 measurements. In collaboration with these results, insets show the digital image of the drop of L-alanine solution on the respective surfaces. In this regard, it was likely the PMMA surface was made moderately hydrophilic due to the presence of SNFs. The result also demonstrated that the SNFs were homogeneously spread on the surface of PMMA using a sputter coater for deposition; similar results were also revealed when the contact angle and surface tension of water were obtained (Supporting Information, Table S1). [Note: silicon isolator was placed on the surface of SNFs-PMMA to afford for the crystallization of multiple solution or assessment of repeated solution in a confined volume of 10 µL].

Surface modified PMMA with SNFs was then characterized using optical spectroscopy. Results obtained can be seen in Figure S1 which shows the absorbance spectra of SNFs-PMMA platform; this result was in accordance to our previous published paper.[13] Inset contains real color photographs of PMMA disk with and without silicon isolator.

Drop (10 µL)	PMMA Contact Angle degrees	Surface Tension (mN/m)	SNFs-PMMA Contact Angle degrees	Surface Tension (mN/m)
L-alanine	62.1 ± 4.0 	23.6 ± 0.4	60.6 ± 1.1 	24.3 ± 0.4
Water	61.4 ± 0.80 	59.1 ± 0.99	36.5 ± 0.22 	27.8 ± 6.4

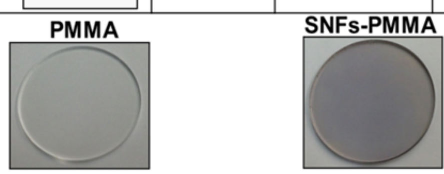


Table S1. Contact angles and surface tension of alanine solution on PMMA and SNFs-PMMA platforms. The insets show the digital image of the drop of alanine solution on the respective surfaces.

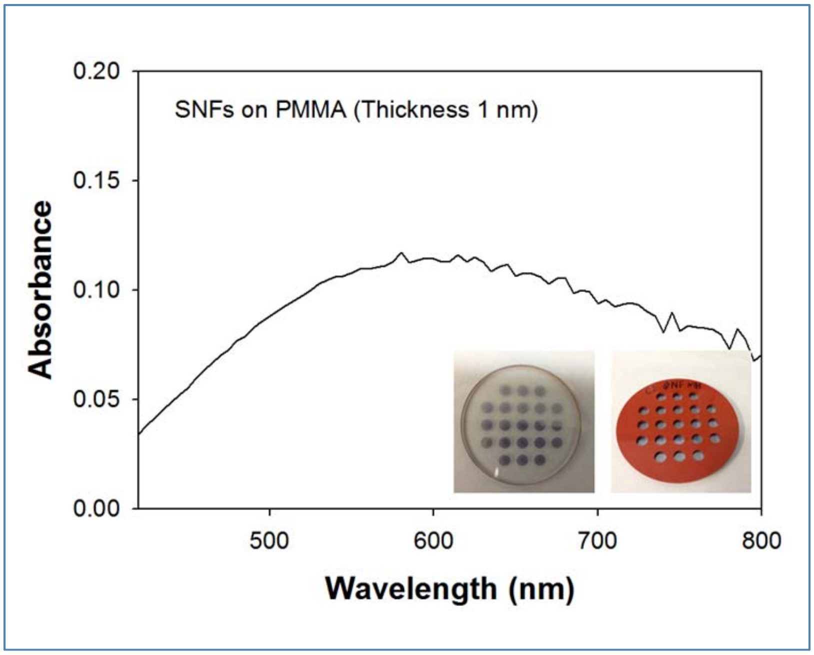


Figure S1. Absorbance spectra of SNFs-PMMA platform (PMMA was used as blank), and real color photographs of PMMA disc with and without silicon isolator.

2. Temperature Measurements during Microwave Heating

Since MA-MAEC technology depends on the generation of a microwave induced temperature gradients, we investigated the temperature of the water, PMMA, and SNFs-PMMA respectively (shown in figure S2). For each experiment, the temperature was measured over the course of 90 minutes of continuous heating in a microwave to simulate the crystallization experiments. SNFs-PMMA proved to have the lowest final temperature; this result is in agreement with silver's cooling ability when carrying out MA-MAEC.

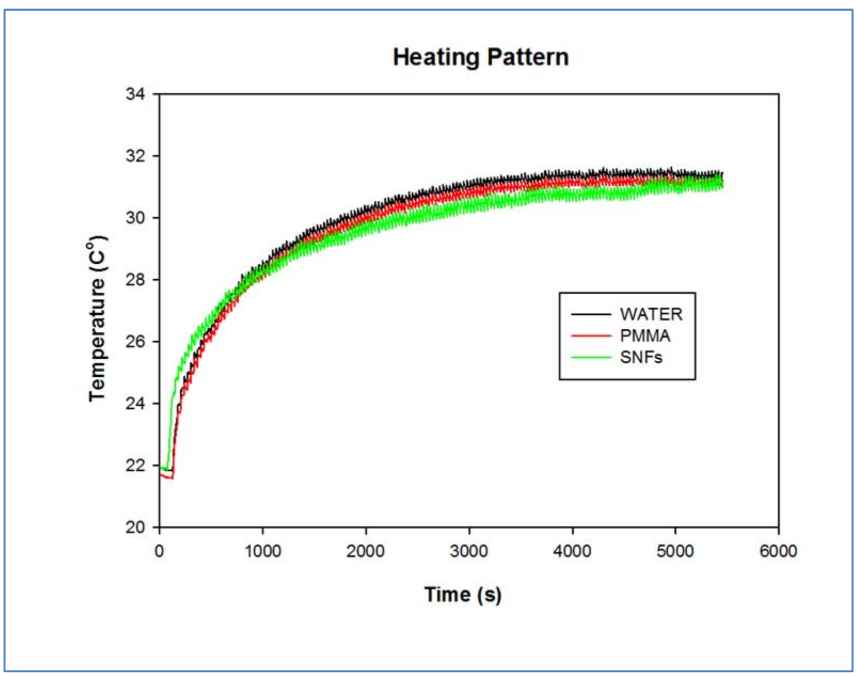


Figure S2. Actual temperature measurements for water, PMMA surface, and SNFs-PMMA surface, respectively.

3. Characterization of crystals

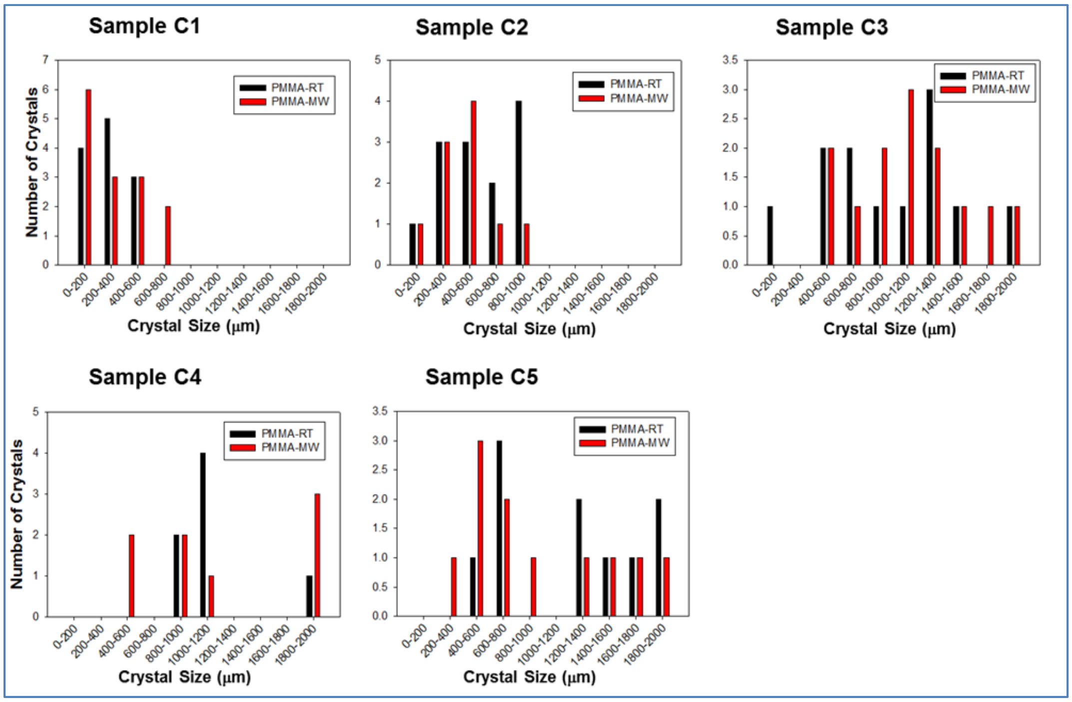


Figure S3. Crystal size and number of crystals of alanine on PMMA at room temperature and using microwave heating (Samples C1-C5).

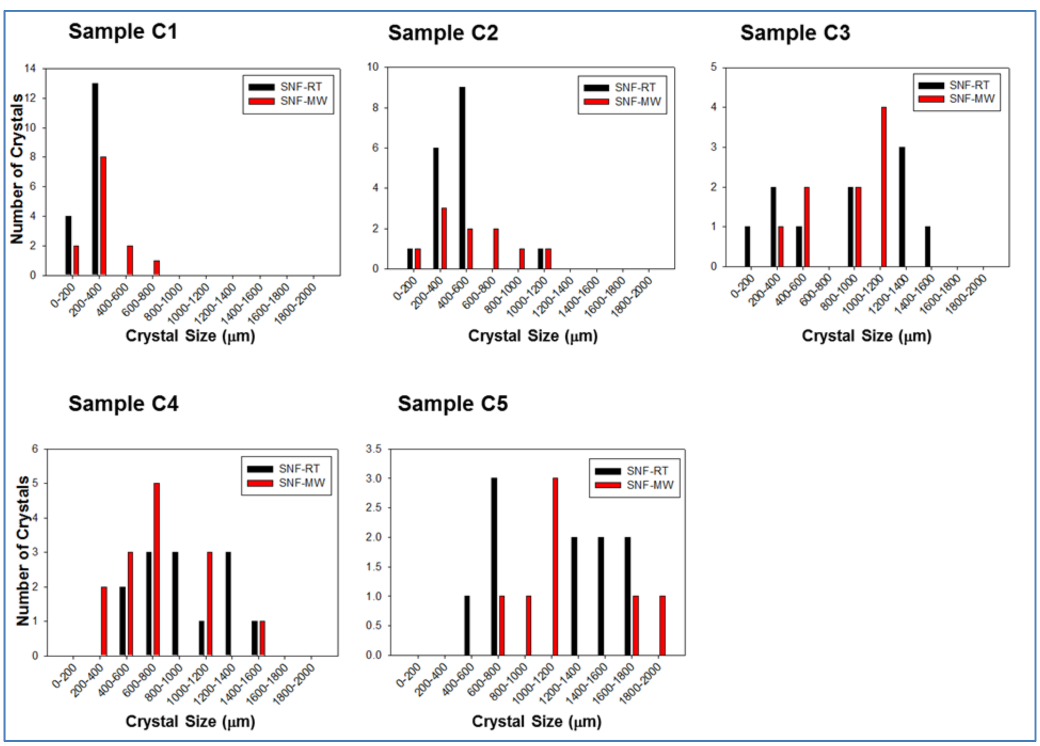


Figure S4. Crystal size and number of crystals of alanine on SNFs-PMMA at room temperature and using microwave heating (Samples C1-C5).

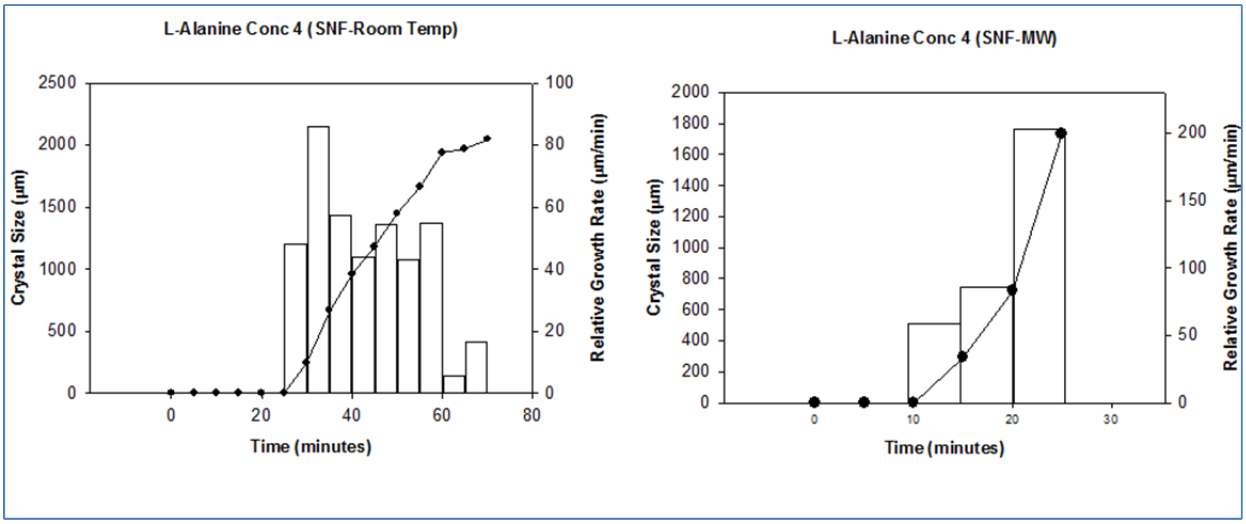


Figure S5. Crystal size and relative growth rate of L-Alanine crystals on SNFs-PMMA from sample C4 at room temperature and using microwave heating.

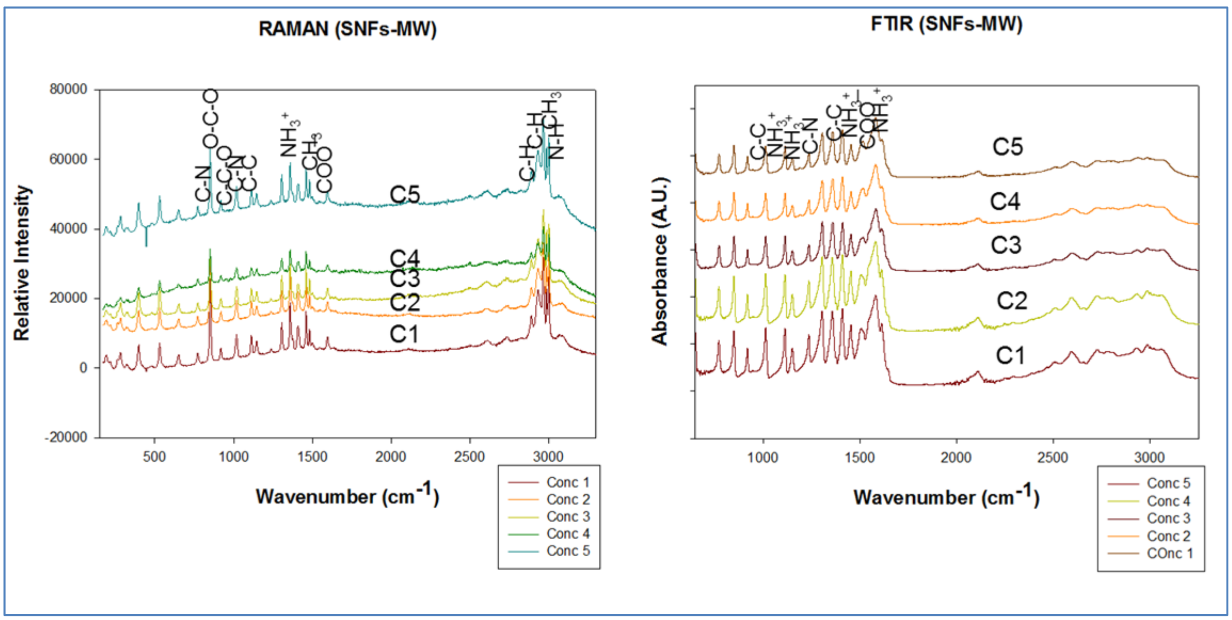


Figure S6. Raman and Fourier Transform Infrared spectra of L-alanine crystals on SNF-PMMA platform using microwave heating (Sample C1-C5).

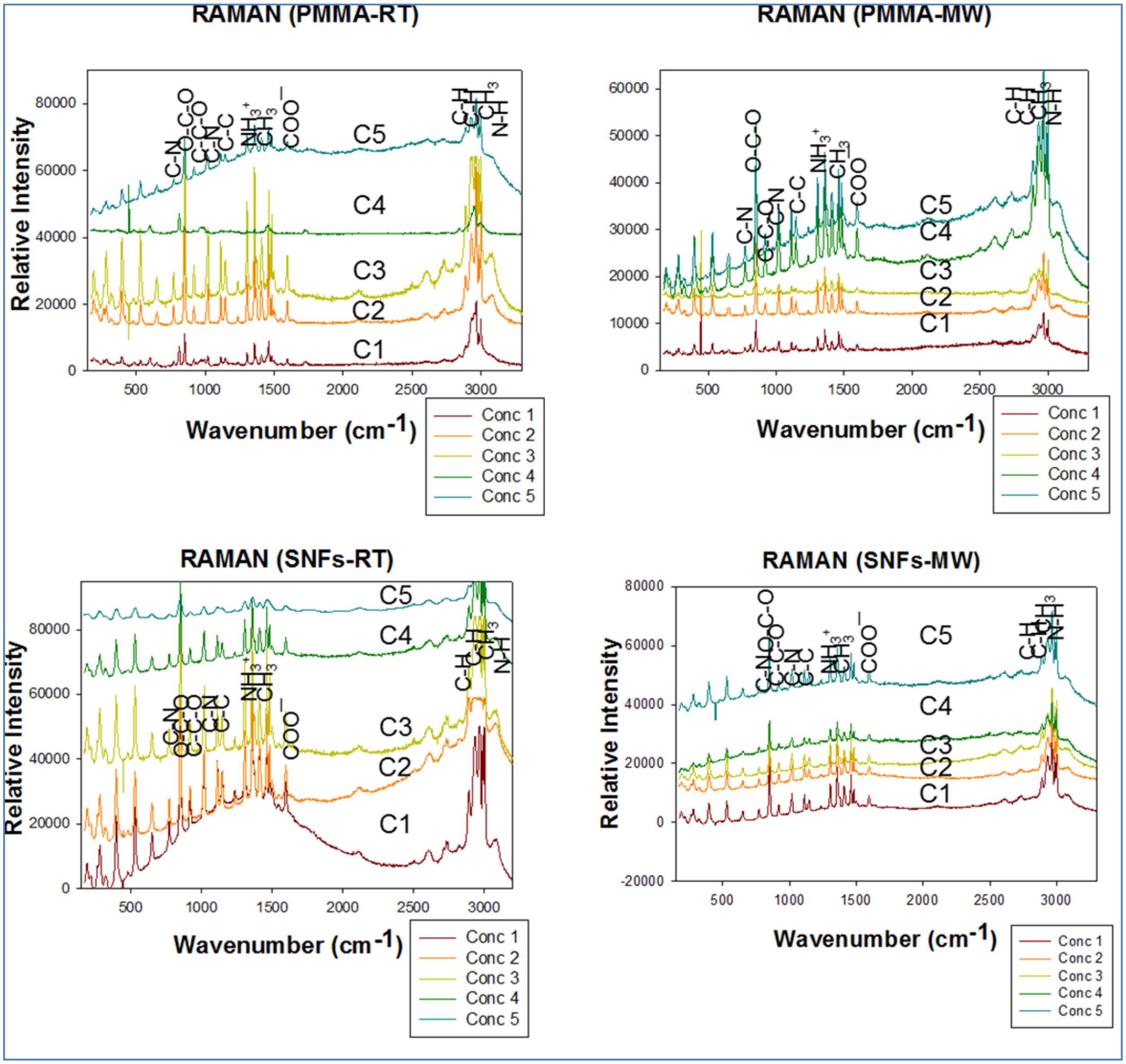


Figure S7. Raman spectra of L-alanine crystals on blank PMMA and SNFs-PMMA platform at room temperature and using microwave heating (Samples C1-C5).

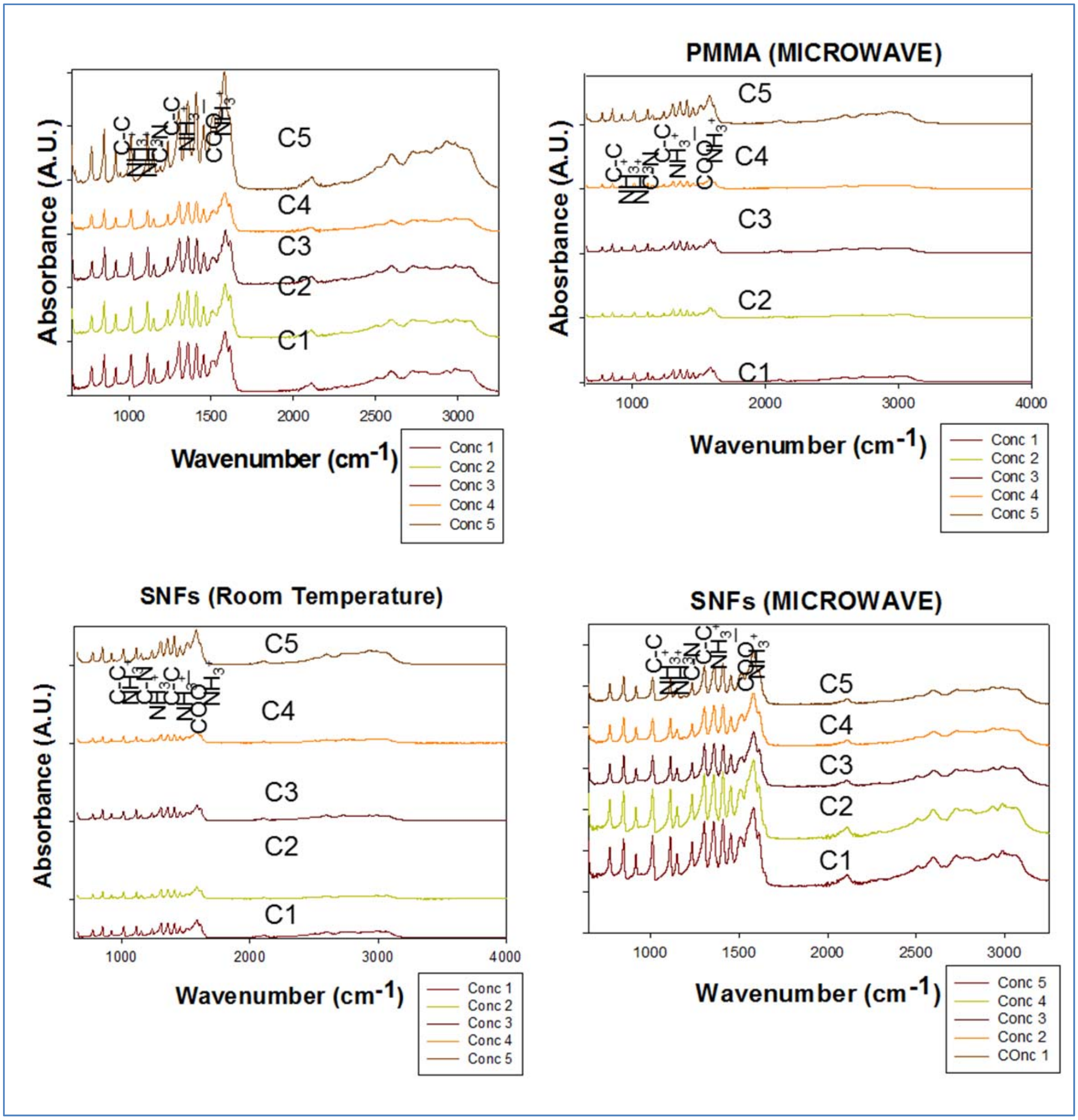


Figure S8. Fourier Transform Infrared spectra of L-alanine crystals on blank PMMA and SNFs-PMMA platform at room temperature and using microwave heating (Samples C1-C5).

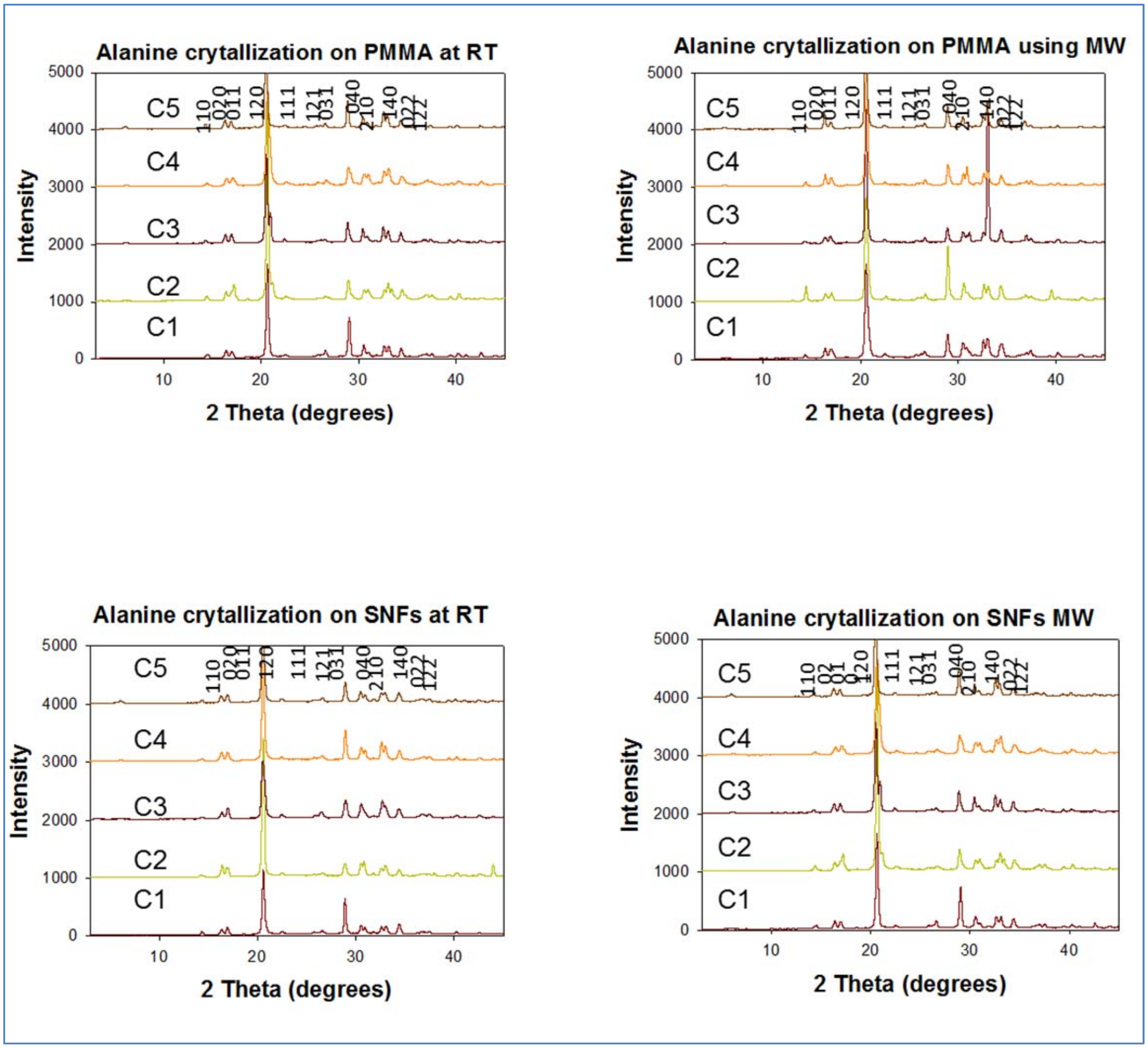


Figure S9. Powder X-ray diffraction of L-alanine crystals on blank PMMA and SNFs-PMMA platform at room temperature and using microwave heating (Samples C1-C5).

4. Simulations

In this work, the effect of L-leucine on the crystallization of L-alanine was further investigated using theoretical simulations (Materials Studio™) in conjunction with our experimental PXRD and optical microscopy data. The experimental PXRD data was uploaded into Material Studio™ and the known peaks from the diffraction pattern for our samples were selected to simulate the crystal morphology. The simulated L-alanine crystals and those observed experimentally using optical microscopy are shown in Figure S9. The comparison between the optical images and the simulated crystals allowed us to identify the faces of L-alanine crystals grown from all samples. One can see that L-alanine crystals generated through theoretical simulations bear a significant resemblance to L-alanine crystals grown experimentally from samples C1-C5. For example, L-alanine crystals grown without L-leucine (sample C1) have a mixture of three major shapes as shown in Figure S10, where the identity of all faces are not immediately clear to non-experts in the field. In this regard, theoretical simulations based on experimental PXRD data afforded for the identification of all 7 major crystal faces of the L-alanine (sample C1, without L-leucine). Theoretical simulations and experimental data for sample C2 show that {110} and {020} faces grew larger as compared to {120} face with the addition of 8.50% (w/w) of L-Leucine. As the extent of L-leucine was increased in samples C3-C5, the {110} and {020} faces grew even larger than the {120} face. The structural differences between the L-alanine crystals grown from each sample can directly be attributed to the amount of L-leucine added to L-alanine. The direct evidence for this observation can be found in sample C5, where the amount of L-leucine additive was the largest of all conditions being studied, the longest crystals ranging from 350-2089 µm were observed. This proves that the inhibition of growth rate of the {120} face on L-alanine is proportional to the amount of L-leucine additive.

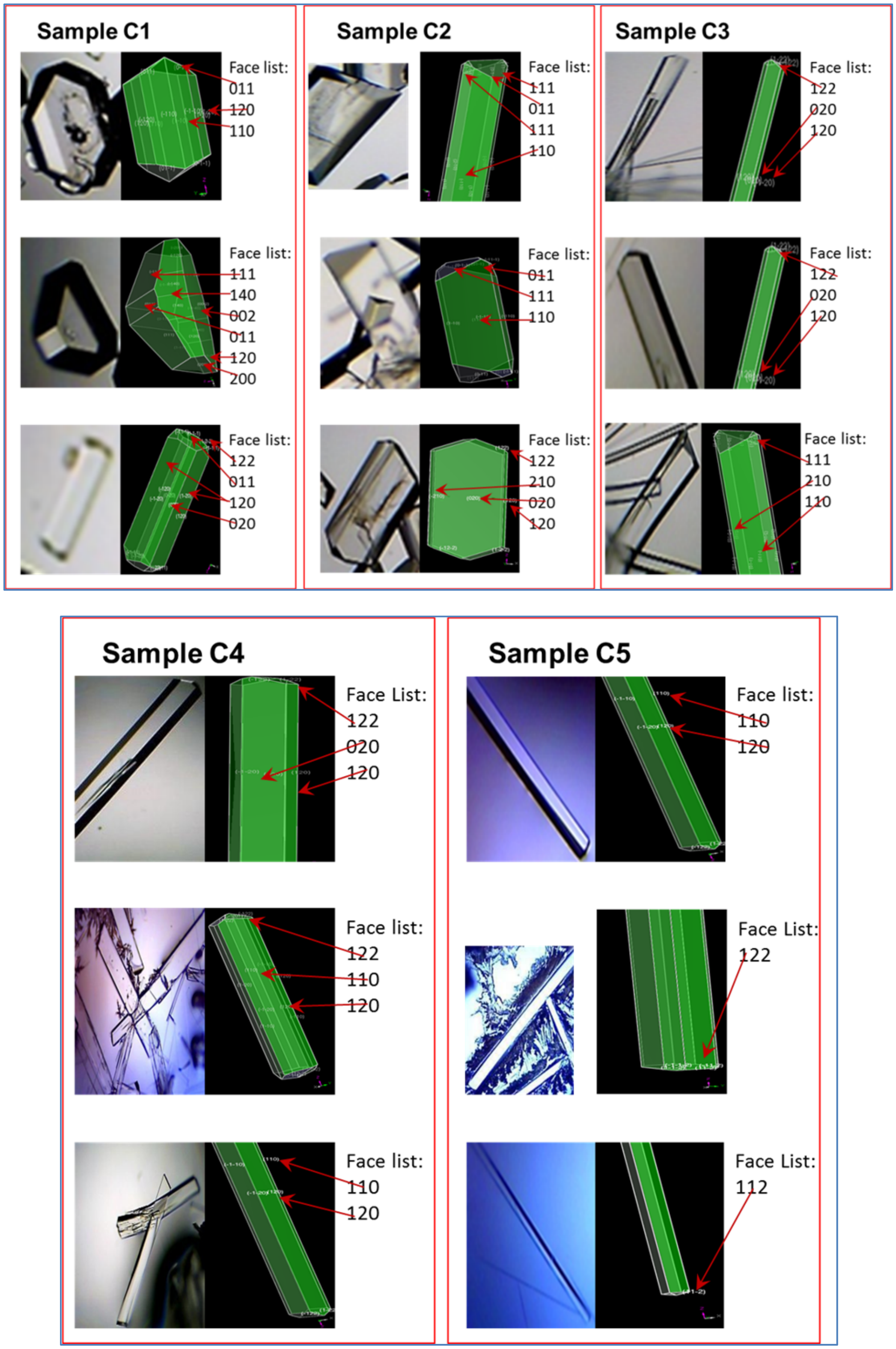


Figure S10. Comparison of L-alanine crystals grown from samples C1-C5 experimentally and using theoretical simulations.