Effect of nucleants in photothermally assisted crystallization

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Supplementary Information

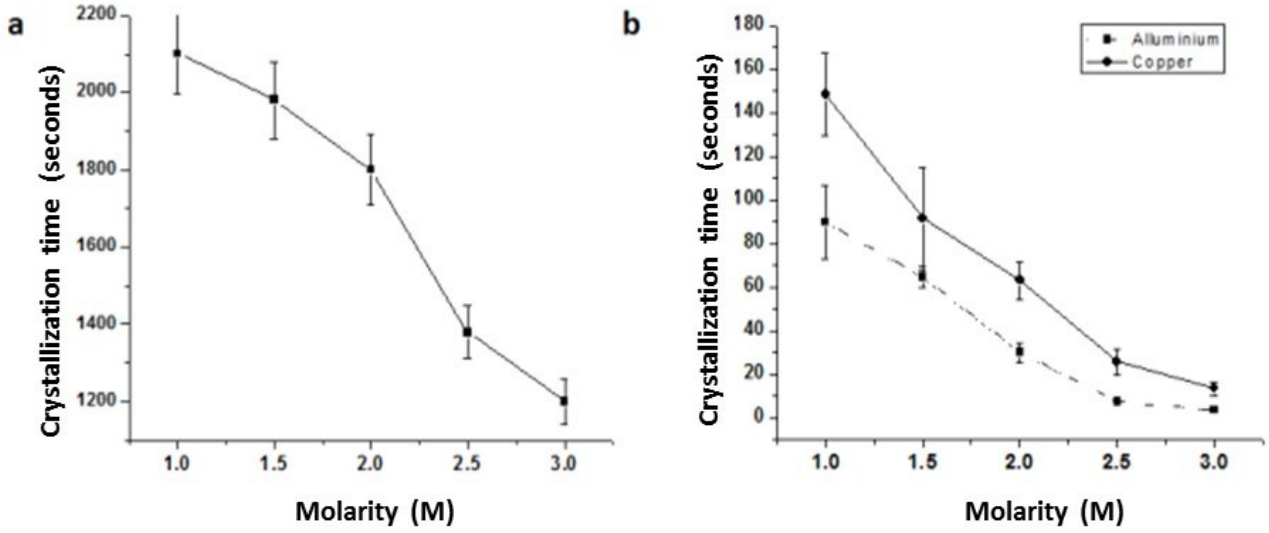

Figure 1. Effect of concentration on crystallization time. The time required to obtain crystals for different concentrations of glycine is shown in (a) control (b) under laser with copper as well as aluminum wire.

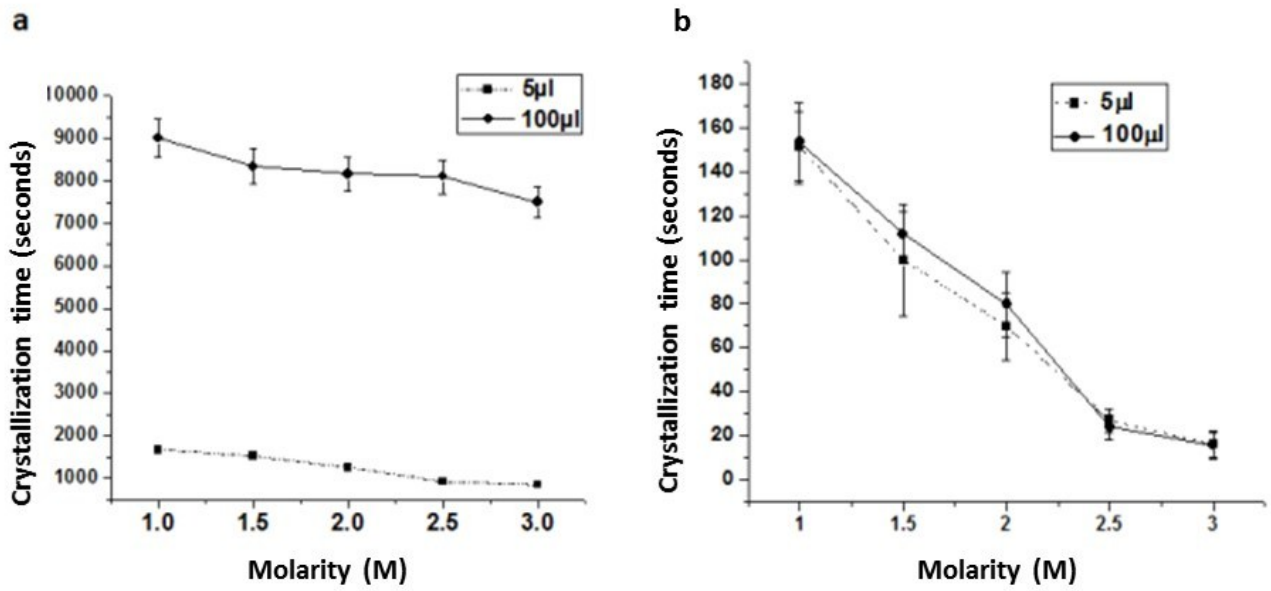

Figure 2. Effect of drop size on crystallization time. Crystallization time with respect to different sample volume for various concentrations of glycine is shown in (a) control, (b) under laser with copper wire. For the clarity purpose, only 5 µl and 100 µl is drop sizes are shown.

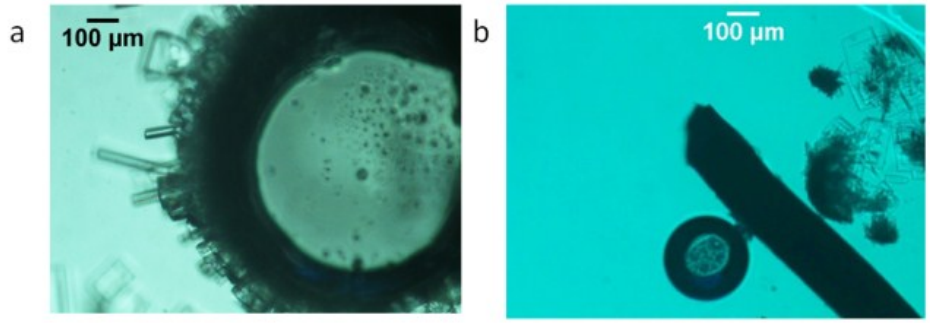

Figure 3. (a) Glycine crystal formation on the surface of the bubble, (b) Crystal formation away from the bubble.

Figure 4: Laser-induced glycine crystal formed around the nucleant aluminum wire

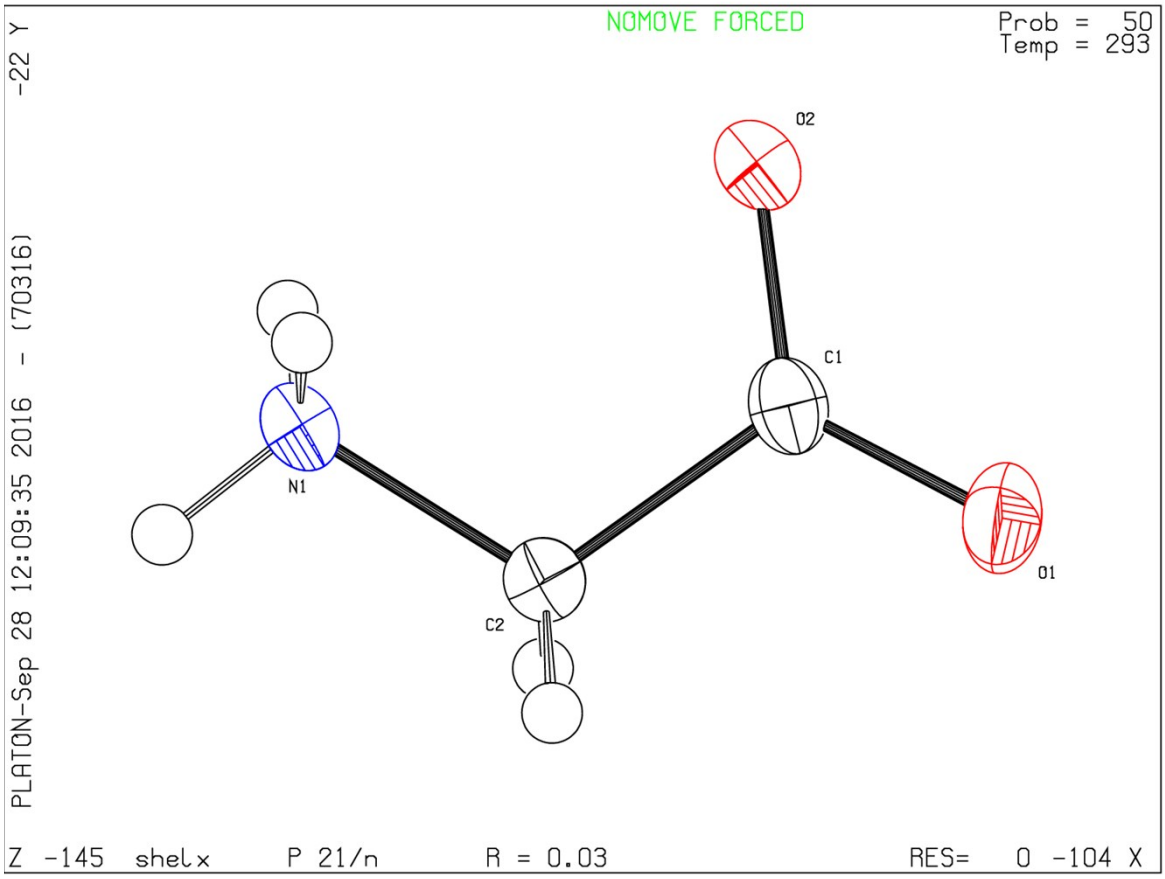

Figure 5: The structure of α-glycine, showing 50% probability displacement ellipsoid and the atom-numbering scheme.

Table 1. Laser-induced crystallization results of various concentrations of NaCl and KCl with copper wire (~0.4 mm x 0.03 mm). The time duration is shown in seconds.

NaCl			KCl		
Molarity	Control	Laser with Cu wire	Molarity	Control	Laser with Cu wire
1 *M*	1800 ± 82	83 ± 5	1 *M*	7785 ± 967	104 ± 17
2 *M*	1320 ± 99	51 ± 5	2 *M*	6600 ± 443	38 ± 6
3 *M*	1260 ± 28	27 ± 1	3 *M*	4605 ± 670	26 ± 8
4 *M*	1140 ± 268	24 ± 11	4 *M*	2475 ± 150	6 ± 0.5
5 *M*	1020 ± 35	10 ± 4	5 *M*	2145 ± 596	4 ± 0.2

Table 2. Comparison of literature data on laser-induced crystallization of glycine with the current study. For comparison and uniformity purpose, laser intensity was used instead of average laser power.

Sl. No.	Source Parameters		Sample details			Time taken to crystallize in (seconds)
	Source	Laser intensity	Concentration (*M*)	H_2O /D_2O	Aged / Fresh	
Pulsed Laser (150 fs, λ = 800 nm)						
1	Femto second[1]	19 PW/cm^2	3	H_2O	Exposed to laser after 5-8 days	600
Pulsed Laser (9 ns, λ = 106 4nm)						
2	Q-switched Nd:YAG[2]	0.7 GW/cm^2	2.69	H_2O	Exposed to laser after 5-8 days	1800
3	Q-Switched Nd:YAG[3]	0.4 GW/cm^2	4	H_2O	Exposed to laser after 3 days	After several hours
Continuous Wave λ = 1064nm						
4	Nd:YVO_4[4]	0.4 GW/cm^2	2	D_2O	3 h	415
5	Nd:YAG[5] (+ Gold thin film)	8.9 MW/cm^2	3	H_2O	Fresh	122
6	Nd:YVO_4[6] (+SWCNT)	6.82 MW/cm^2	3	H_2O	Fresh	15
7	Nd:YAG (current study with cooper & aluminum)	0.8 MW/cm^2	3	H_2O	Fresh	3
8	Nd:YAG (current study with graphite)	0.1 MW/cm^2	3	H_2O	Fresh	3

Table 3. Raman bands and assignments for α-glycine, and γ -glycine single crystals in the spectral region of 200-3050 cm^{-1}.

Raman Frequencies		Assignments
α-glycine	γ -glycine	
360	366	CCN rock
486	---	NH_3 tor, C-C bend
502	502	CO_2 wag
602	606	CO_2 bend
697	688	CO_2 bend, C-N bend
889	890	C-C str
918	921	CH_2 rock
1034	1048	C-N str, CCN asym str
1109	1109	CH_2 rock
---	1129	NH_3 rock
1139	1137	NH_3 rock
---	1156	NH_3 rock
1324	1325	CH_2 twist
---	1337	CH_2 wag
---	1344	CH_2 wag or tor
1410	1395	CO_2 sym str
1437	1436	CH_2 sci
1453	---	CH_2 sci
1512	1496	NH_3 sym def
1565	1573	CO_2 asym str
1669	1673	NH_3 asym def
2972	2962	CH_2 sym str
3006	2998	CH_2 asym str

Table 4. Raman bands and assignments for lysozyme single crystal in the spectral region of 450-1800 cm^{-1}.

Raman Frequencies	Assignments	Raman Frequencies	Assignments
459		1028	Phe
492		1071	ν(C-N)
506	ν(S-S) ggg	1088	ν(C-N)
525	ν(S-S) ggt	1099	
541	ν(S-S)	1124	ν(C-N)
574	Trp	1177	Tyr
621	Phe	1193	Tyr
643	Tyr	1208	Tyr, Phe
695	Met: ν(C-S)	1236	Amide III
721	Cys: ν(C-S)	1257	Amide III
759	Trp	1334	Trp
835	Tyr	1360	Trp
855	Tyr	1425	
871	Trp	1449	$\delta(CH_2)$
876	Trp	1458	$\delta(CH_3)$
898	ν(C-C)	1549	Trp
930	ν(C-C)	1576	Phe
961		1619	Tyr
976		1638	
1000	Phe	1656	Amide I (α-helix)
1008	Trp	1672.6	Amide I (β-sheet)

Abbreviations: ν-stretching, Phe-Phenylalanine, Trp-Tryptophan, Tyr-Tyrosine, Met-Methionine

Table 5 .Crystallographic and geometric data of α-glycine crystal obtained using a laser with nucleant comparison with literature values.

	Current Study	Literature[7]
Empirical formula	$C_2H_5NO_2$	$C_2H_5NO_2$
Wavelength	0.71075 Å	0.71075 Å
Crystal system & Space group	Monoclinic & $P2_1/n$	Monoclinic & $P2_1/n$
Unit cell dimensions: a, b, c(Å)	5.1014(8), 11.957(2), 5.4649(9)	5.087(2),11.73(3),5.460(2)
α, β, γ (°)	90, 111.842(8),90	90, 111.990(15), 90
Volume & Z	309.42(9) $Å^3$ & 4	303.21(18) $Å^3$ & 4
Density (calculated)	1.612 Mg/m^3	1.645 Mg/m^3
Absorption coefficient	0.143 mm^{-1}	
F(000)	160	
Crystal size	0.360 x 0.230 x 0.220 mm^3	
Theta range for data collection	3.408 to 27.485°	
Index ranges	-6<=h<=6,-15<=k<=15,-6<=l<=7	
Independent reflections	709 [R(int) = 0.0396]	
Completeness to theta = 25.242°	100.0 %	
Final R indices [I>2sigma(I)]	R1 = 0.0333, wR2 = 0.0962	
R indices (all data–3601 reflections)	R1 = 0.0376, wR2 = 0.0977	
Extinction coefficient	0.21(2)	
Largest diff. peak and hole	0.256 and -0.207 $e.Å^{-3}$	
Bond Length (Å)		
O(2)-C(1)	1.2508(17)	1.2599(5)
C(1)-O(1)	1.2468(16)	1.2575(5)
C(1)-C(2)	1.5264(18)	1.5269(6)
C(2)-N(1)	1.4760(17)	1.4823(6)
Bond Angle (°)		
O(1)-C(1)-O(2)	125.67(12)	125.54(2)
O(1)-C(1)-C(2)	117.34(12)	117.44(2)
O(2)-C(1)-C(2)	116.99(12)	117.01(2)
N(1)-C(2)-C(1)	111.92(11)	111.49(2)
Torsion Angle (°)		
O(1)-C(1)-C(2)-N(1)	-18.54(16)	19.54(2)
O(2)-C(1)-C(2)-N(1)	161.86(11)	-161.31(2)

Table 6: Comparison of crystallographic data for α-glycine with data extracted from CSD

Sl. No.	CCDC number	a(Å)	b(Å)	c(Å)	α(°)	β(°)	γ(°)	Space group	Volume Å^3	R factor
1	***Current study***	***5.1014(8)***	***11.957(2)***	***5.4649(9)***	***90***	***111.842(8)***	***90***	**$P2_1/n$**	***309.42(9)***	***0.0376***
2	1416370	5.0855(3)	11.8018(8)	5.4600(4)	90	111.973(1)	90	$P2_1/n$	303.895	0.0279
3	1416373	5.124(6)	12.042(14)	5.496(7)	90	111.647(14)	90	$P2_1/n$	315.204	0.0431
4	1169354	5.1020(8)	11.9709(17)	5.4575(15)	90	111.70(2)	90	$P2_1/n$	309.698	0.0630
5	1169355	5.1054(6)	11.9688(19)	5.4645(9)	90	111.70(1)	90	$P2_1/n$	310.248	0.0320
6	1169356	5.1054(6)	11.9688(19)	5.4645(9)	90	111.697	90	$P2_1/n$	310.254	0.0400
7	1169357	5.1020(8)	11.9709(17)	5.4575(15)	90	111.705	90	$P2_1/n$	309.687	0.0450
8	1169369	5.0835(10)	11.820(2)	5.4579(9)	90	111.95(2)	90	$P2_1/n$	304.176	0.0300
9	193596	5.0993(3)	11.9416(6)	5.4608(3)	90	111.784(2)	90	$P2_1/n$	308.783	0.0371
10	193597	5.0999(3)	11.9516(6)	5.4594(3)	90	111.781(2)	90	$P2_1/n$	309.005	0.0267
11	193598	5.1008(3)	11.9558(8)	5.4602(3)	90	111.772(3)	90	$P2_1/n$	309.233	0.0273
12	193599	5.1012(3)	11.9651(9)	5.4604(4)	90	111.763(5)	90	$P2_1/n$	309.528	0.0300
13	193600	5.1026(3)	11.9752(9)	5.4602(4)	90	111.757(5)	90	$P2_1/n$	309.876	0.0311
14	193601	5.1074(3)	12.0775(9)	5.4596(4)	90	111.827(5)	90	$P2_1/n$	312.63	0.0314
15	1169372	5.106(1)	11.979(5)	5.463(2)	90	111.75(2)	90	$P2_1/n$	310.355	0.0274
16	1169373	5.1047(3)	11.9720(14)	5.4631(3)	90	111.740(5)	90	$P2_1/n$	310.122	0.0370
17	842907	5.0993(3)	11.9416(6)	5.4608(3)	90	111.784(2)	90	$P2_1/n$	308.783	NA
18	849671	5.1038(3)	11.9701(4)	5.4620(2)	90	111.718(4)	90	$P2_1/n$	310.003	0.0477
19	849670	5.1040(10)	11.966(2)	5.4620(11)	90	111.79(3)	90	$P2_1/n$	309.754	0.0462
20	849669	5.1012(3)	11.9376(6)	5.4626(7)	90	111.848(1)	90	$P2_1/n$	308.758	0.0502
21	849668	5.1150(10)	11.925(2)	5.4812(11)	90	111.80(3)	90	$P2_1/n$	310.424	0.0470
22	849667	5.0936(1)	11.8783(2)	5.4625(1)	90	111.872(10)	90	$P2_1/n$	306.709	0.0451
23	849666	5.0949(1)	11.8776(2)	5.4614(3)	90	111.899(7)	90	$P2_1/n$	306.65	0.0337
24	849665	5.0906(1)	11.8413(2)	5.4605(1)	90	111.935(1)	90	$P2_1/n$	305.327	0.0445
25	849664	5.0912(1)	11.8353(2)	5.4617(1)	90	111.981(3)	90	$P2_1/n$	305.177	0.0369
26	849663	5.0876(1)	11.8092(2)	5.4615(1)	90	111.992(1)	90	$P2_1/n$	304.254	0.0395
27	849662	5.0881(1)	11.7980(1)	5.4629(1)	90	112.034(1)	90	$P2_1/n$	303.983	0.0389
28	849661	5.0856(1)	11.7821(2)	5.4615(1)	90	112.029(1)	90	$P2_1/n$	303.357	0.0370
29	849660	5.0874(2)	11.7817(5)	5.4635(7)	90	112.053(1)	90	$P2_1/n$	303.514	0.0343
30	986786	5.1042(8)	11.9718(2)	5.93652(9)	90	121.2642(8)	90	$P2_1/n$	310.081	NA

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