SUPPORTING INFORMATION:

Interfacial Functional Terminals Enhance the Heterogeneous Nucleation of Lysozyme Crystals

XPS and ATR-FTIR spectra were carried out to determine the chemical compositions and functional groups on different substrate surfaces. Table S1 lists elemental compositions in the surfaces of S-PhAc, S-biPh and S-PhCF$_3$. Combining with XPS spectra (Fig. S1), it is indicated that the extra carbon species (located at 288.06 eV) in the surface of S-PhAc are due to O=C-NH groups [1], while for S-biPh the sulfur species at 168.05 eV is attributed to O=S=O groups, [2] and for S-PhCF$_3$ the fluorine species at 687.96eV is due to the groups of CF$_3$.[3]

Table S1 Element compositions of substrates with different functional groups.

Sample	Element Content (atomic%)					
	C	N	O	Si	S	F
Amino	26.78	3.25	47.92	22.05	/	/
S-PhAc	59.76	5.69	22.53	9.35	2.37	/
S-biPh	52.83	6.50	25.95	11.79	2.94	/
S-PhCF$_3$	48.09	7.09	27.42	11.71	2.96	2.53

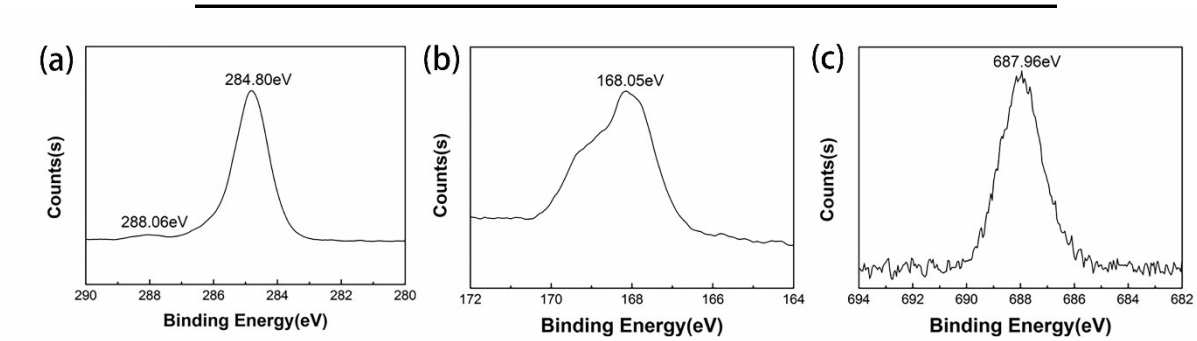

Fig. S1 High resolution XPS spectra of (a) C 1s in S-PhAc, (b) S 2p in S-biPh, and (c) F 1s in S-PhCF$_3$.

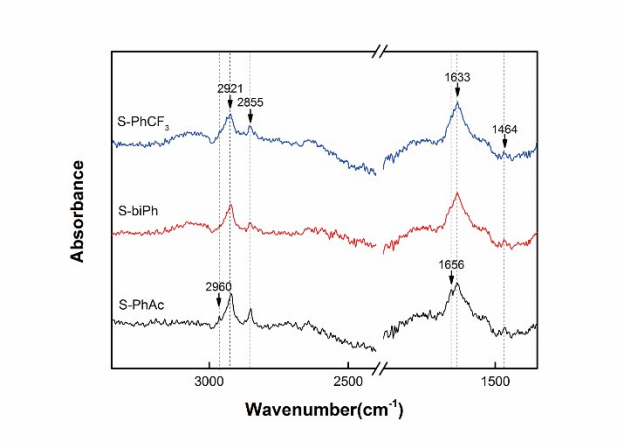

Fig. S2 ATR-FTIR spectra of the coverslips modified with S-PhAc, S-biPh, and S-$PhCF_3$.

As shown in Fig. S2, for three kinds of functional surfaces, major bands are observed at 2921 cm^{-1}, 2855 cm^{-1}, 1633 cm^{-1}, and 1464 cm^{-1}. The peaks at 2921 $cm^{-1}$and 2850 cm^{-1} indicate the asymmetric stretching of C-H in methene.[4] The peaks at 1633 cm^{-1} and 1464 cm^{-1} represent the absorption of C=C in benzene,[5] and aromatics rings,[6] respectively. For S-PhAc, two new bands are observed clearly at 2960 cm^{-1} and 1656cm^{-1}, attributed to the C-H stretching of -CH_3,[7] and C=O stretching, [4] respectively.

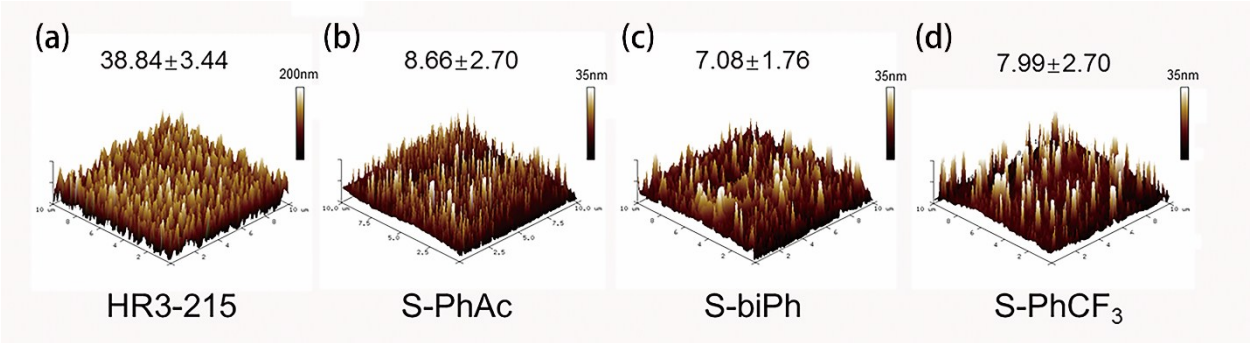

Fig. S3 AFM images of (a) the control coverslip HR3-215, (b) S-PhAc, (c) S-biPh, and (d) S-$PhCF_3$.

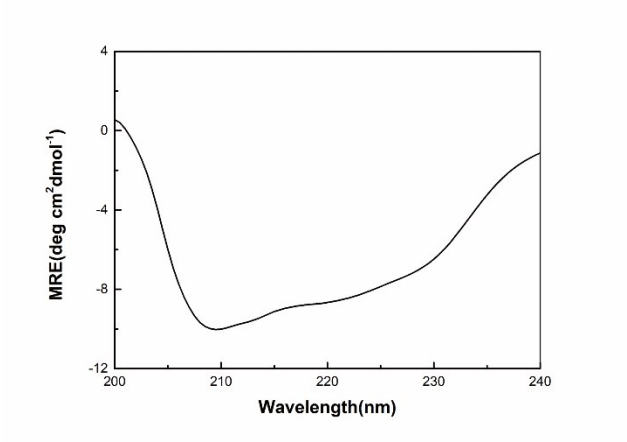

Fig. S4 CD spectra of 100 μg/mL lysozyme aqueous solution containing 0.1 M sodium chloride at room temperature.

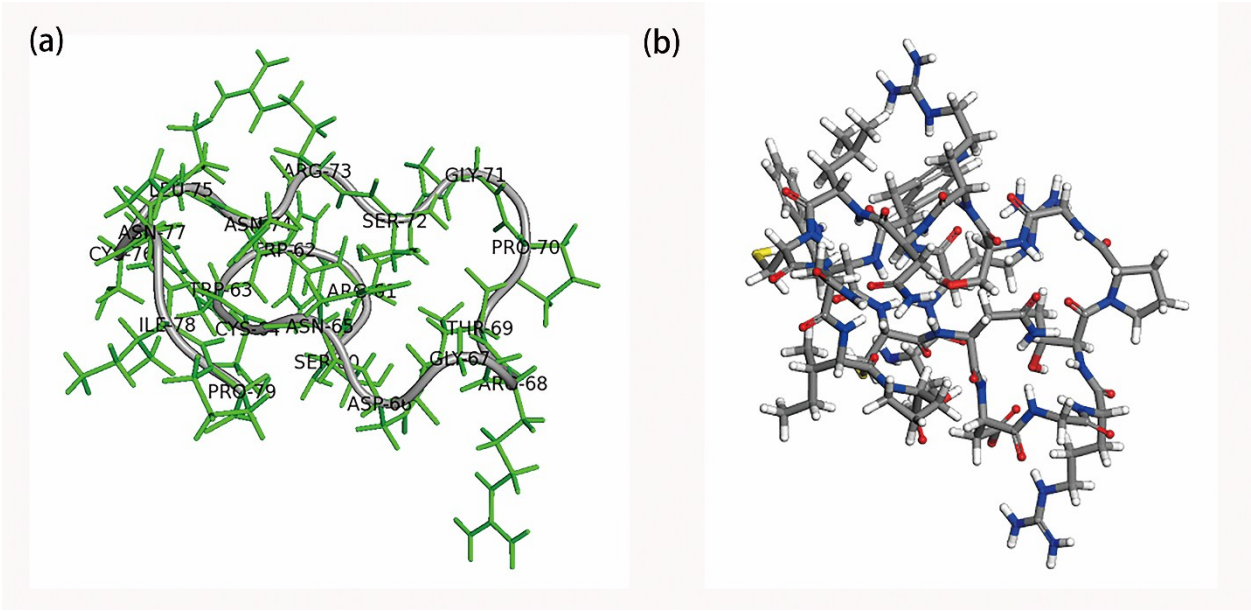

Fig. S5 The structure of the random coiled loop of lysozyme. (a) cartoon model of random coil in grey and the stick model of amino acids in green with the labels of residues identifier, (b) the random structure minimized by COMPASS force fields

Table S2 The binding energies of the coiled lysozyme loop on different functional surfaces.

Surface	E_{total} (KJ/mol)	$E_{surface}$ (KJ/mol)	$E_{random\ coil}$ (KJ/mol)	$\Delta E_{binding}$[a] (KJ/mol)
S-PhAc	-384774.90	-101390.61		-8856.05
S-biPh	-357158.46	-122443.83	9.58	-7335.13
S-PhCF$_3$	-287102.01	-60553.99		-7079.92

[a] The number of functional molecules on the constructed model face is 32 with the coverage ratio of 50 %.

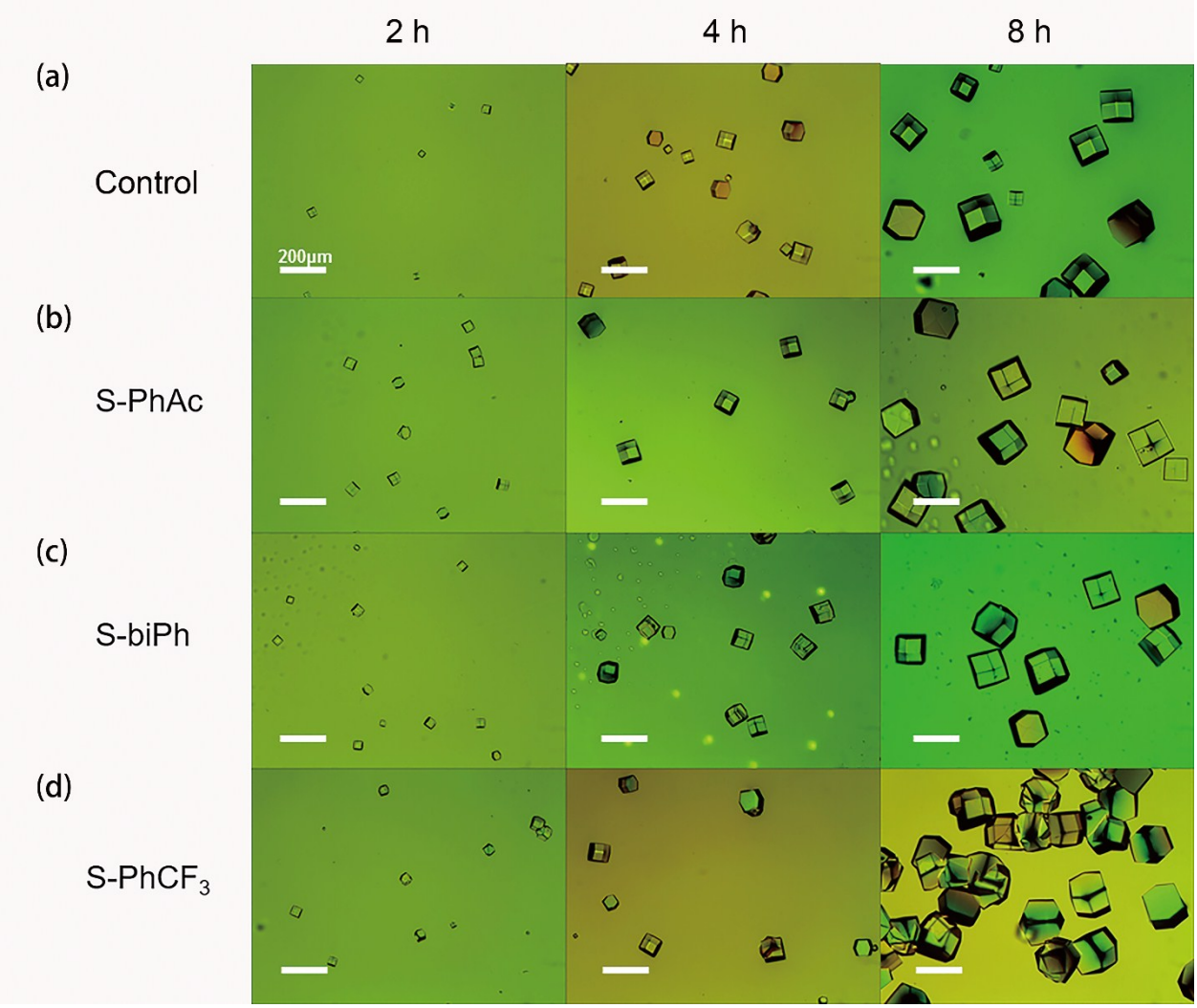

Fig. S6 Photographs of lysozyme crystals grown in 10 mL beakers in the presence of the Control coverslip (a), and in the presence of functional substrate S-PhAc (b), S-biPh (c) or S-$PhCF_3$ (d) at different crystallization time. Scale bar is 200 μm. For each trial, the final solution contained 15 mg/mL lysozyme and 0.6 M sodium chloride.

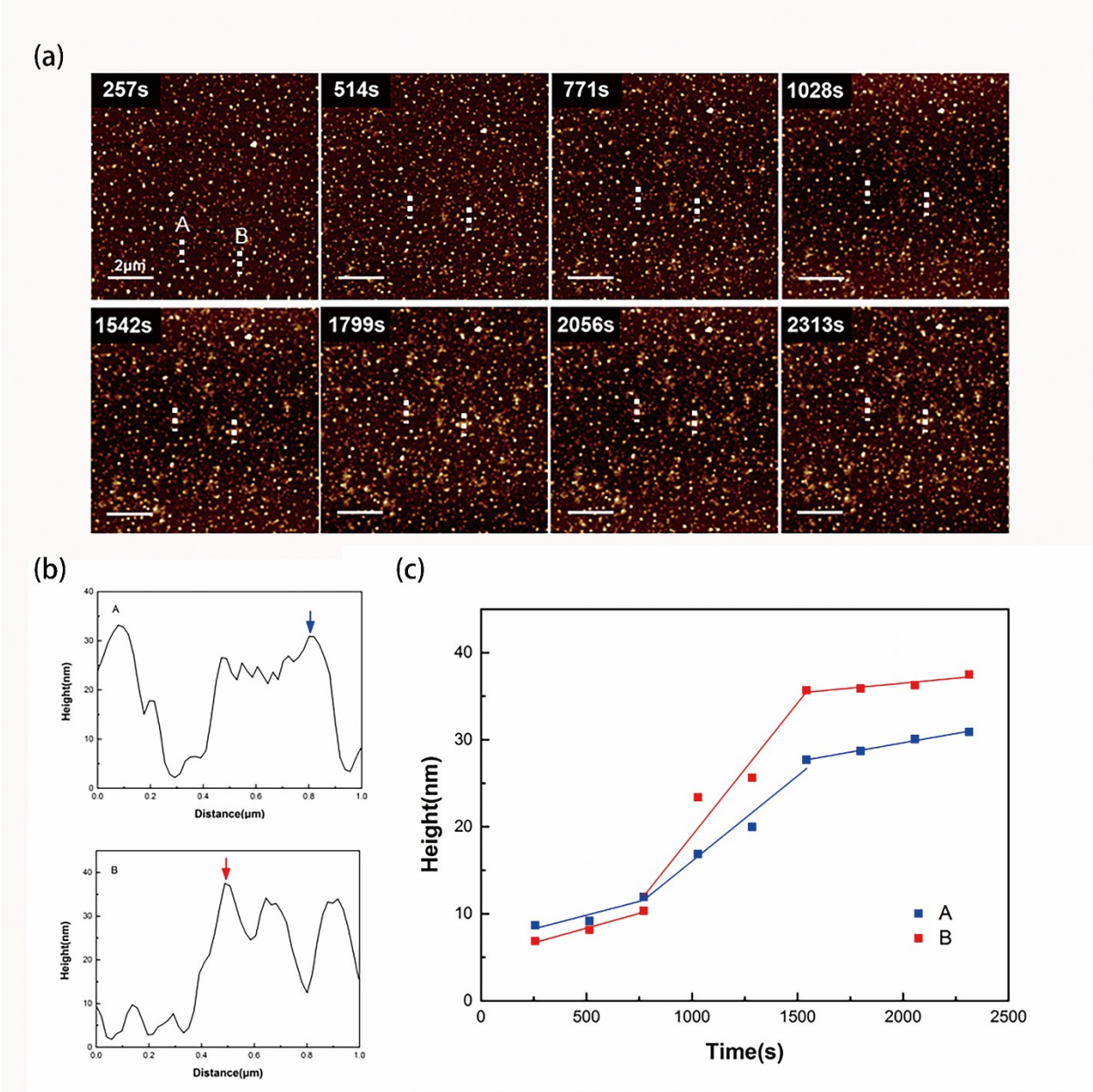

Fig. S7 Time-evolved in situ AFM images of lysozyme crystals grown on the Control coverslip (a), the scale bar is 2 μm. (b) The vertical cross-sections in the height image along the dashed lines in (a). (c) The heights of the arrow-marked peaks in (b) as a function of time.

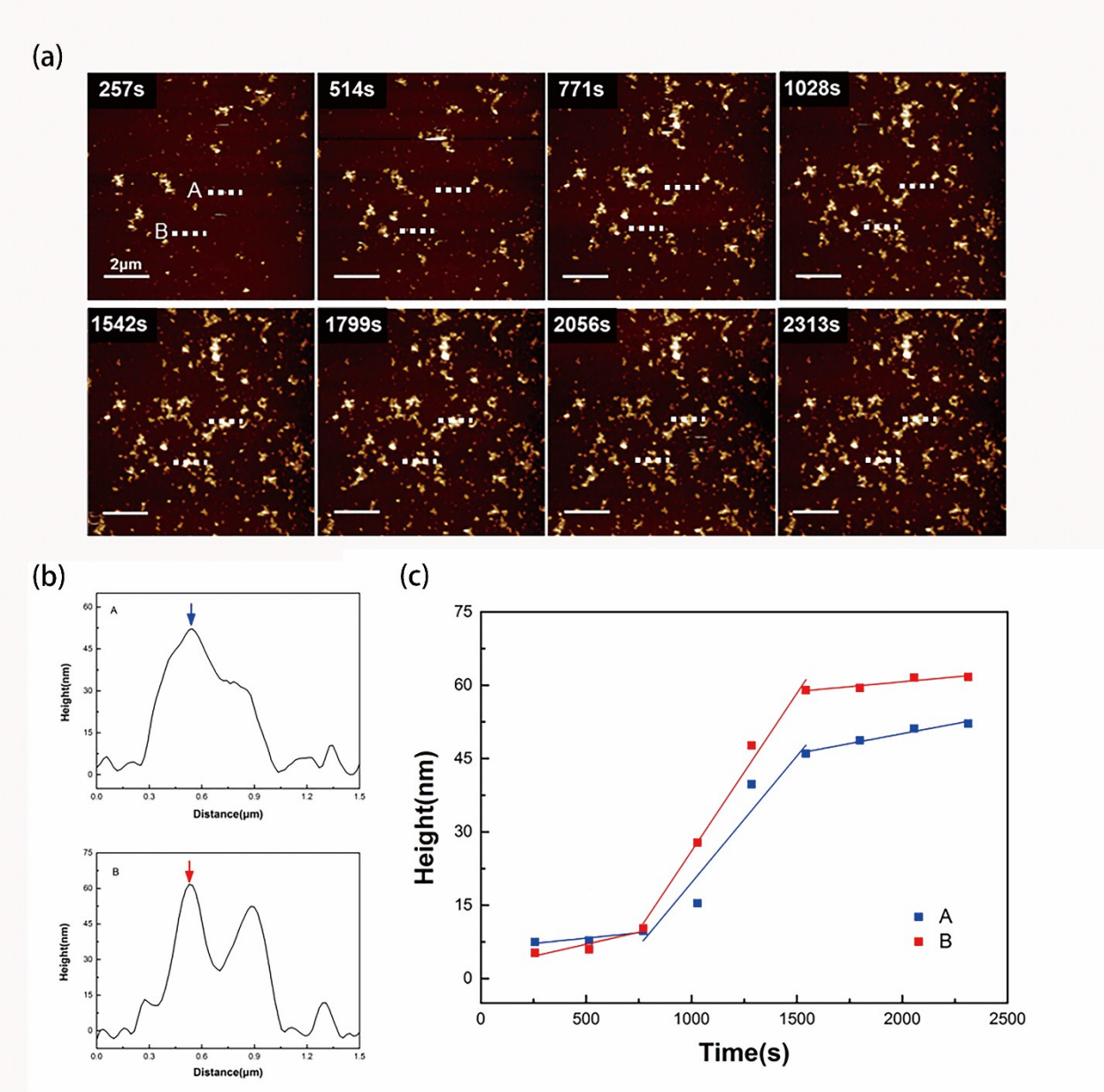

Fig. S8 Time-evolved in situ AFM images of lysozyme crystals grown on S-biPh (a), the scale bar is 2 μm. (b)The vertical cross-sections in the height image along the dashed lines in (a). (c) The heights of the arrow-marked peaks in (b) as a function of time.

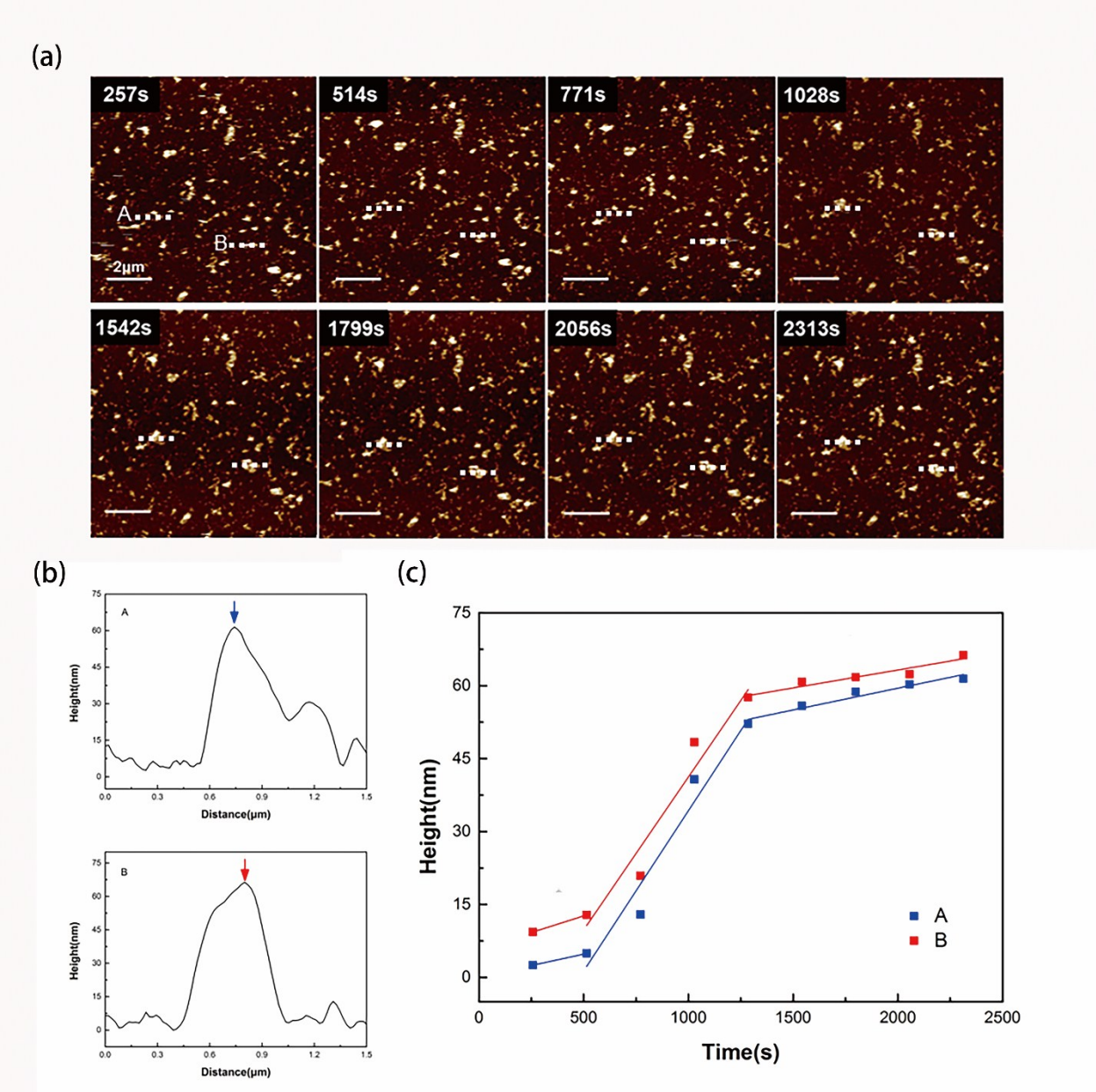

Fig. S9 Time-evolved in situ AFM images of lysozyme crystals grown on S-PhCF$_3$ (a), the scale bar is 2 μm. (b) The vertical cross-sections in the height image along the dashed lines in (a). (c) The heights of the arrow-marked peaks in (b) as a function of time.

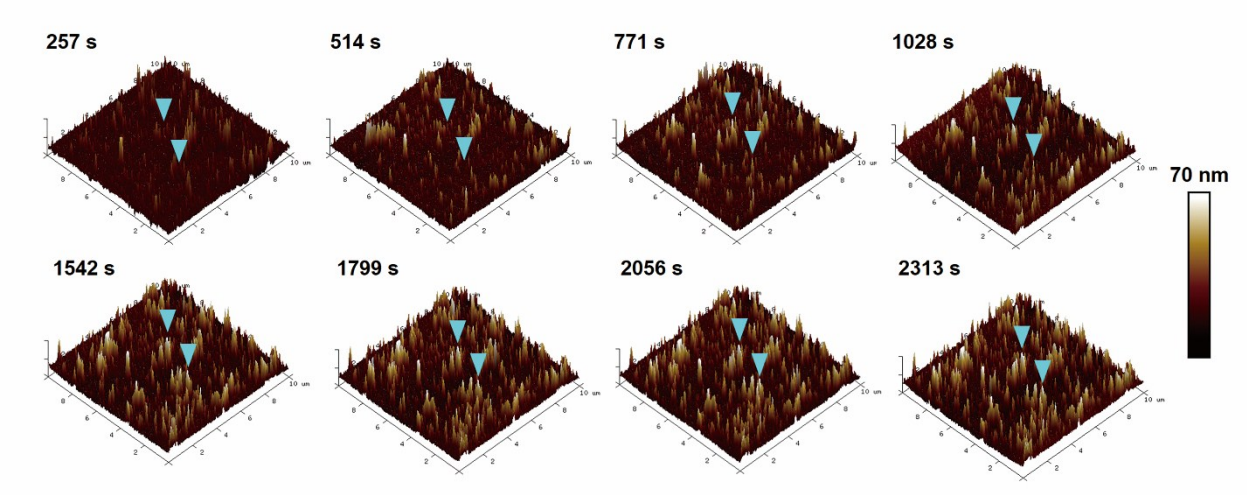

Fig. S10 Time-evolved in situ 3D AFM images of lysozyme crystals grown on the S-PhAc, the blue arrows indicate the positions of points A and B in Fig. 8A of the revised manuscript.

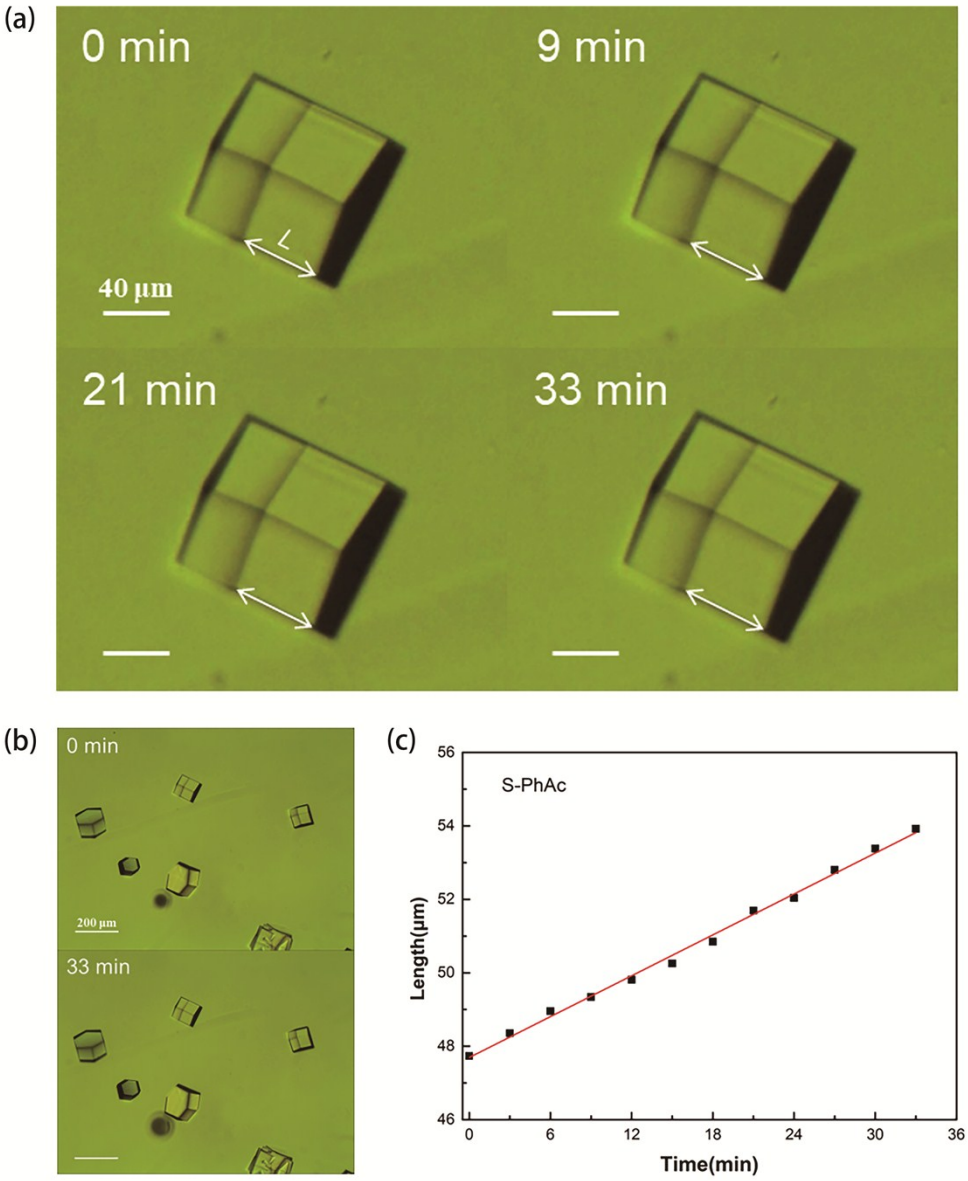

Fig.S11 (a) On the S-PhAc: time-evolved polarizing microscope photographs of lysozyme crystals grown within 33 min after adding the protein solution. Scale bar is 40 μm. (b) Comparing photographs of lysozyme crystals on the S-PhAc at 0 min and 33 min (the scale bar indicates 200 μm). (c) Plots of characteristic length *L* (the length of lysozyme crystals marked by arrow in (a)) as a function of crystallization time.

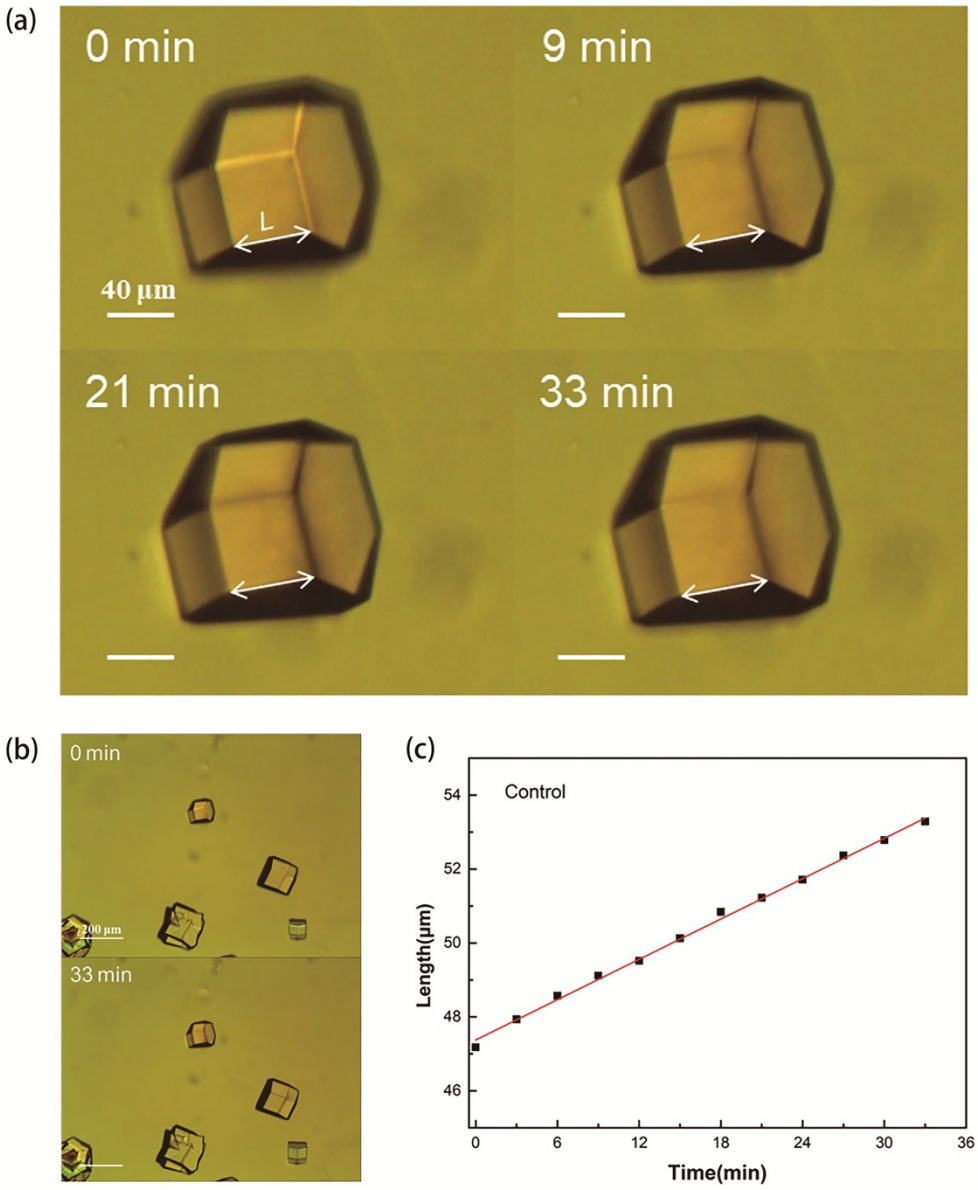

Fig.S12 (a) on the Control coverslip: time-evolved polarizing microscope photographs of lysozyme crystals grown within 33 min after adding the protein solution. Scale bar is 40 μm. (b) Comparing photographs of lysozyme crystals on the Control coverslip at 0 min and 33 min (the scale bar indicates 200 μm). (c) Plots of characteristic length *L* (the length of lysozyme crystals marked by arrow in (a)) as a function of crystallization time.

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