Roll-to-roll fabrication of large scale and regular arrays of three-dimensional nanospikes for high efficiency and flexible photovoltaics

Siu-Fung Leung,[1] Leilei Gu,[1,+] Qianpeng Zhang,[1,+] Kwong-Hoi Tsui,[1] Jia-Min Shieh,[2,*] Chang-Hong Shen,[2] Tzu-Hsuan Hsiao,[2] Chin-Hung Hsu,[2] Linfeng Lu,[3] Dongdong Li,[3] Qingfeng Lin,[1] Zhiyong Fan[1,*]

[+]These authors contributed equally.

[1]Department of Electronic and Computer Engineering, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China SAR

[2]National Nano Device Laboratories (NDL), Hsinchu 30078, Taiwan, ROC

[3]Shanghai Advanced Research Institute, Chinese Academy of Sciences, 99 Haike Road, Zhangjiang Hi-Tech Park, Pudong, Shanghai 201210, China

[*] Corresponding authors: eezfan@ust.hk , jmshieh@narlabs.org.tw

Supplementary:

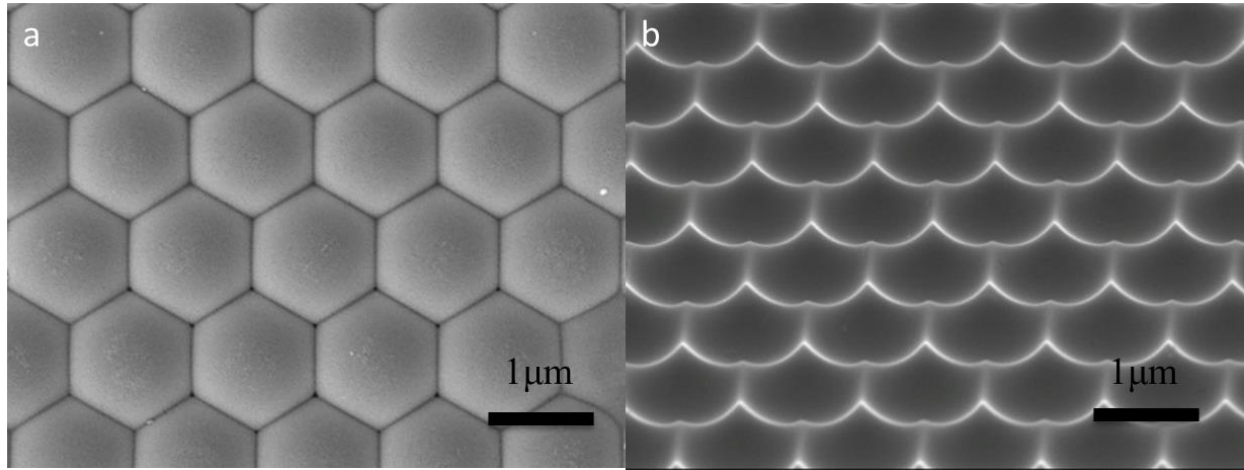**SEM of 3-D Al NSP array substrate and solar cells fabricated on them**

Figure S1: (a) Bottom view of AAO with hexagonal order showing there is no space between each AAO channel. (b) Aluminum texture obtained by hexagonal ordered AAO. Only nano-concave can be form for hexagonal ordered AAO while NSP can be obtained by squarely ordered AAO.
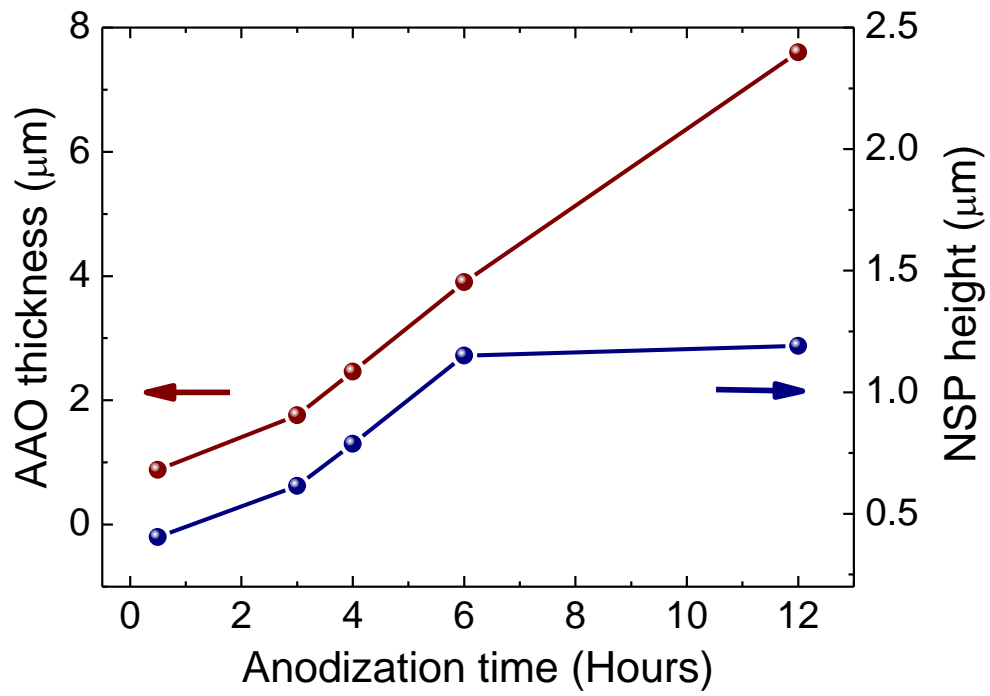
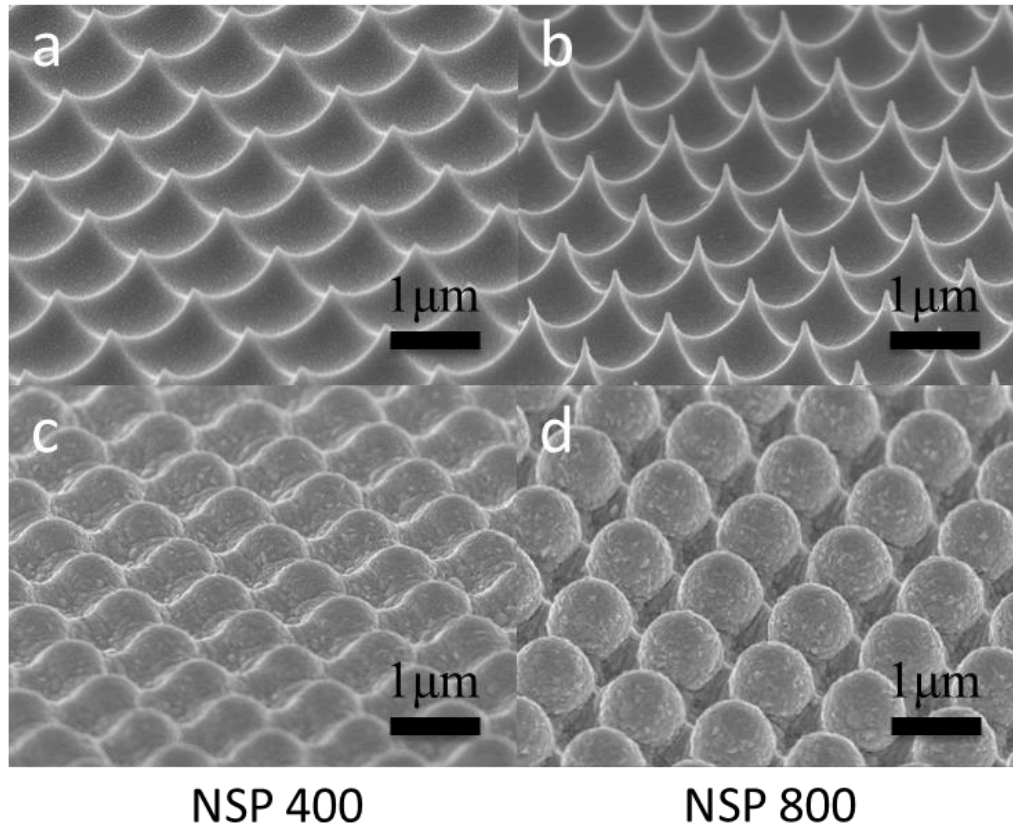**Figure S2**: Relationship of AAO thickness and NSP height with anodization time

Figure S3: 60 degree tilted view SEM image of NSP array of (a) NSP 400, (b) NSP 800 and surface of solar cell fabricated on (c) NSP 400 (75 degree tilted) and (d) NSP 800.
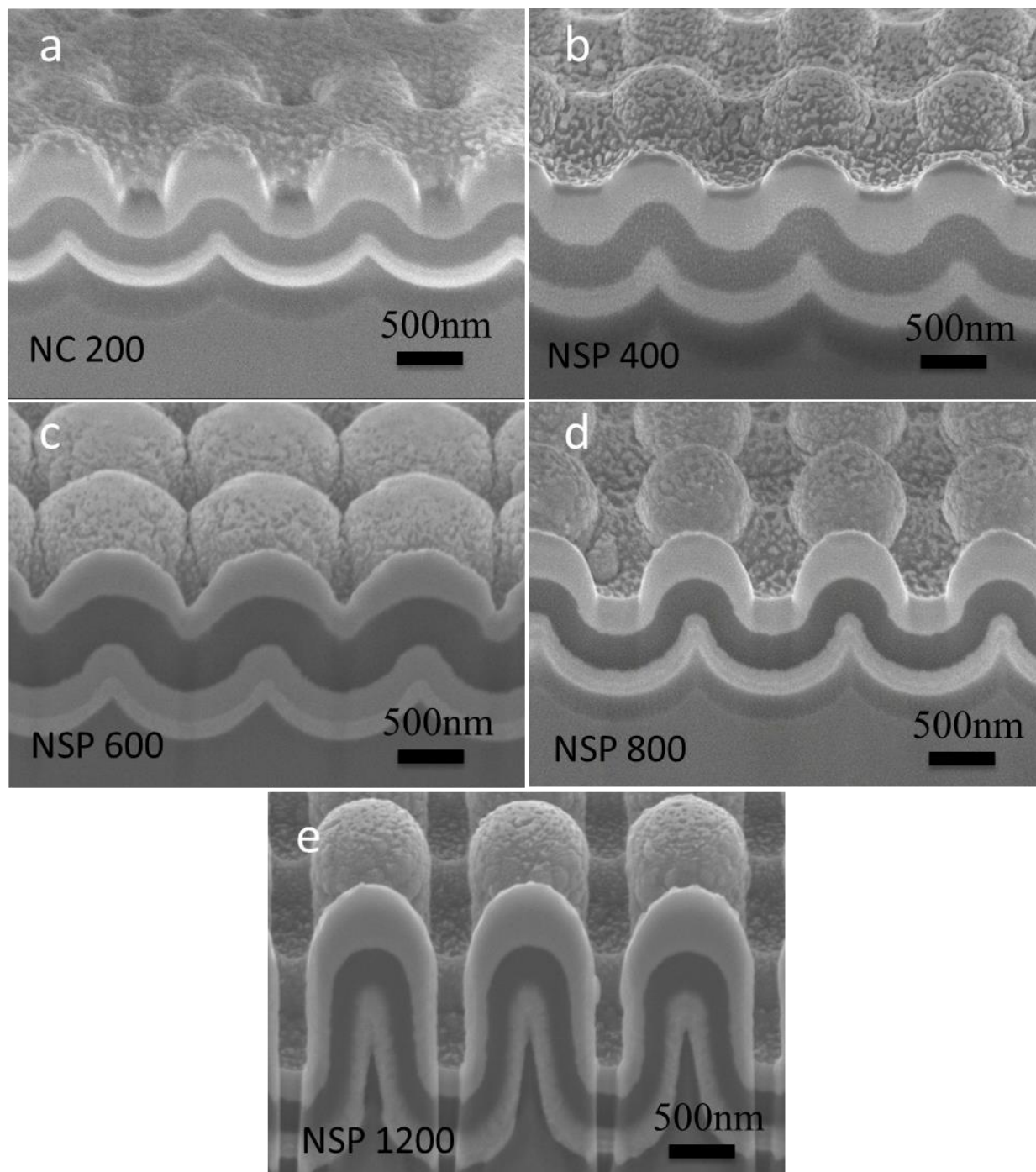
Figure S4: Cross-sectional SEM image of solar cell on (a) NC 200, (b) NSP 400, (c) NSP 600, (d) NSP 800 and (e) NSP 1200

a

b

c

1μm

1μm

1μm
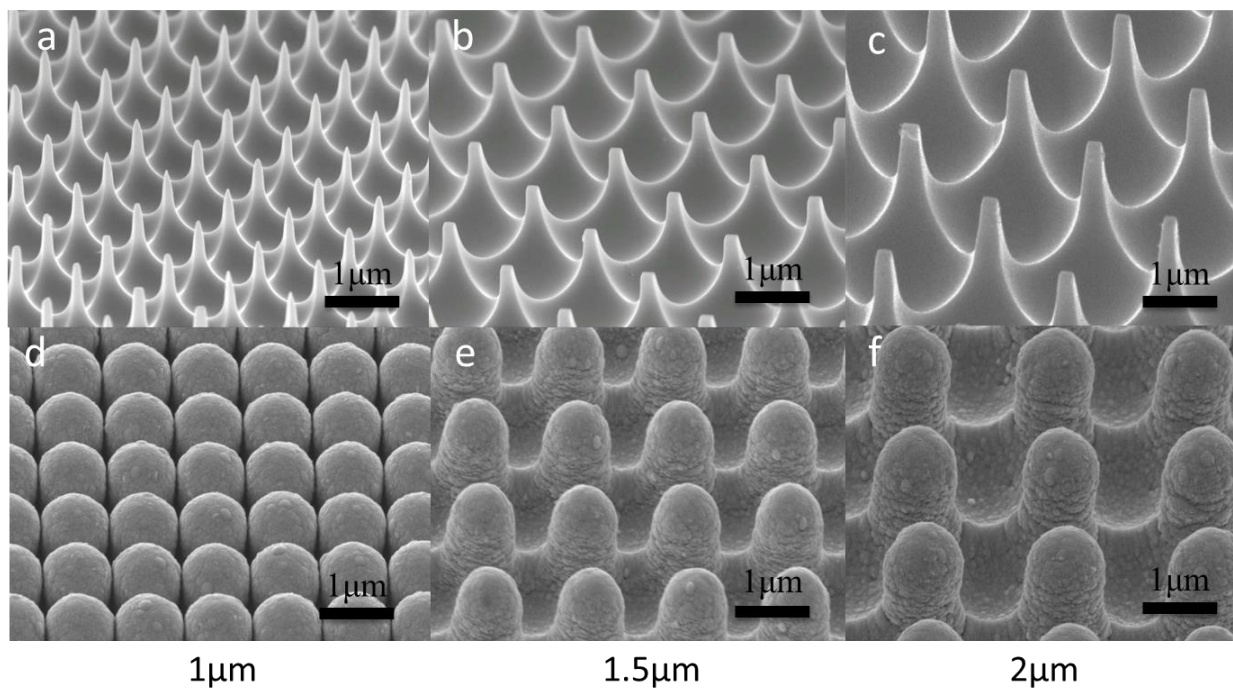
d

e

f

1μm

1μm

1μm

1μm

1.5μm

2μm

Figure S5: 60-degree tilted view SEM image of NSP with pitch (a) 1 μm, (b) 1.5 μm, (c) 2 μm and solar cell fabricated on them were shown respectively on (d), (e) and (f).

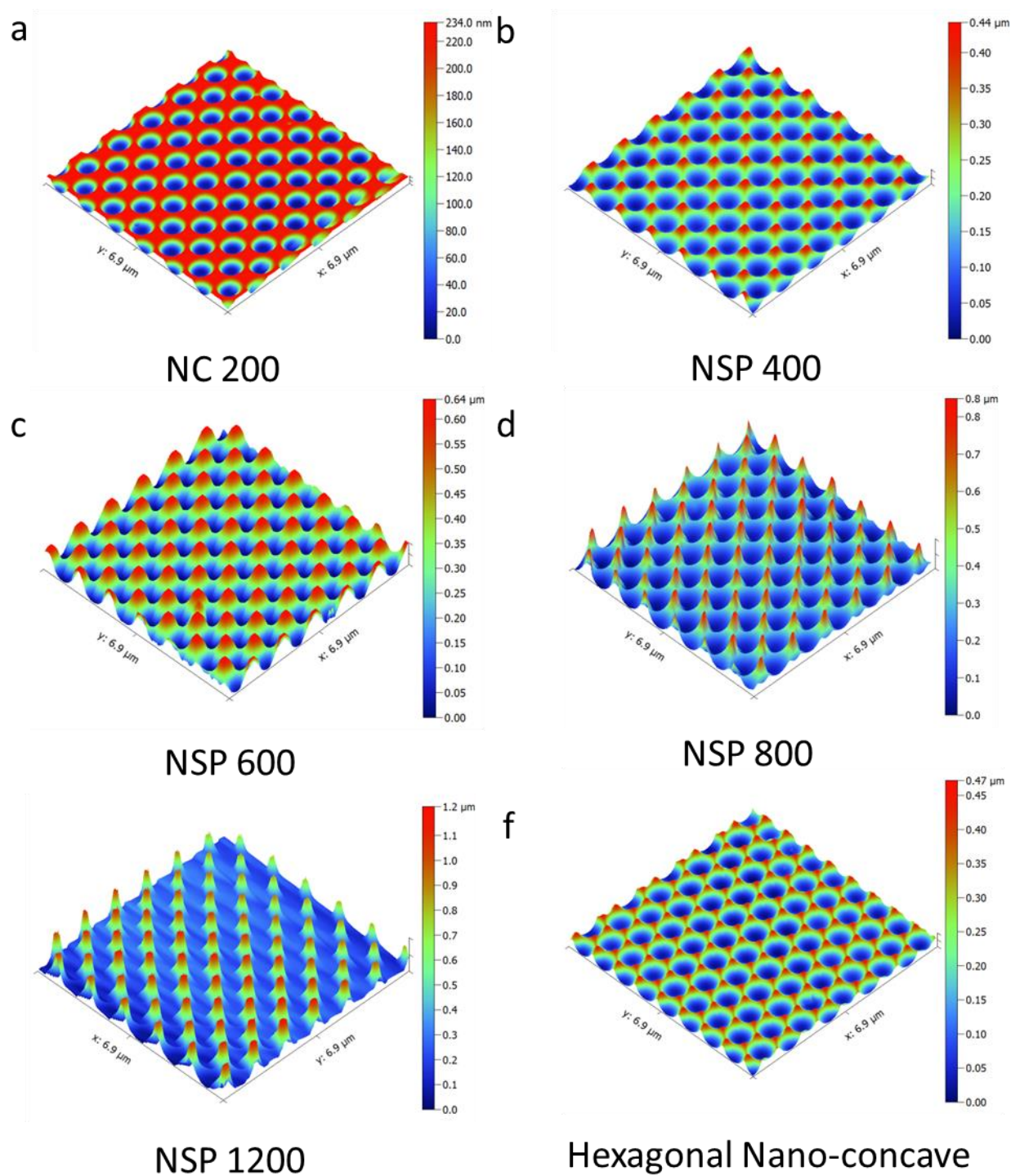# AFM Surface analysis of 3-D Al NSP array substrate

Figure S6: AFM image of (a) NC 200, (b) NSP 400, (c) NSP 600, (d) NSP 800, (e) NSP 1200

and (f) texture by hexagonal nanoconcave.

P. S. The AFM probe cannot fully follows the contours of NSP 800 and NSP 1200 due to the high aspect ratio NSP and resulted in asymmetric shape of the NSP and "flat bottom" in the AFM images of NSP 1200. The depth of the valley of NSP 1200 is around 250nm and therefore the estimated height of NSP of NSP 1200 is 1200nm.
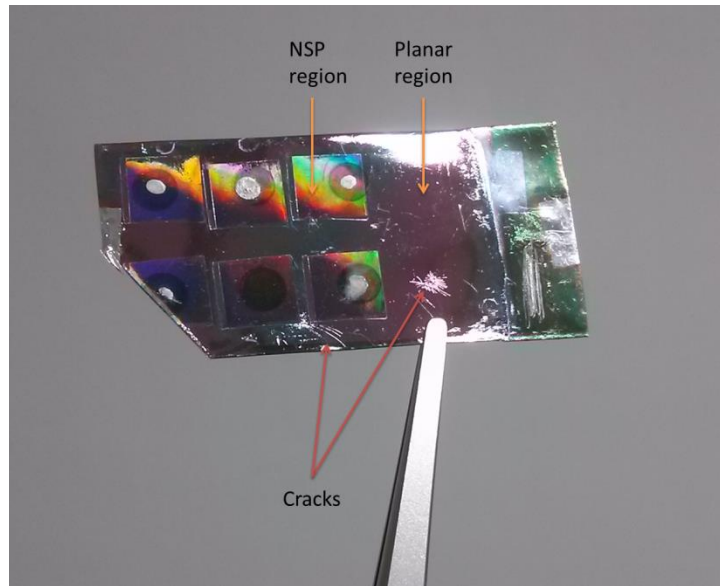
Figure S7: Optical Image of a sample with 6 small scale NSP solar cell indicating cracks appeared on the planar region of the sample, while crack problem do not affect the NSP region.

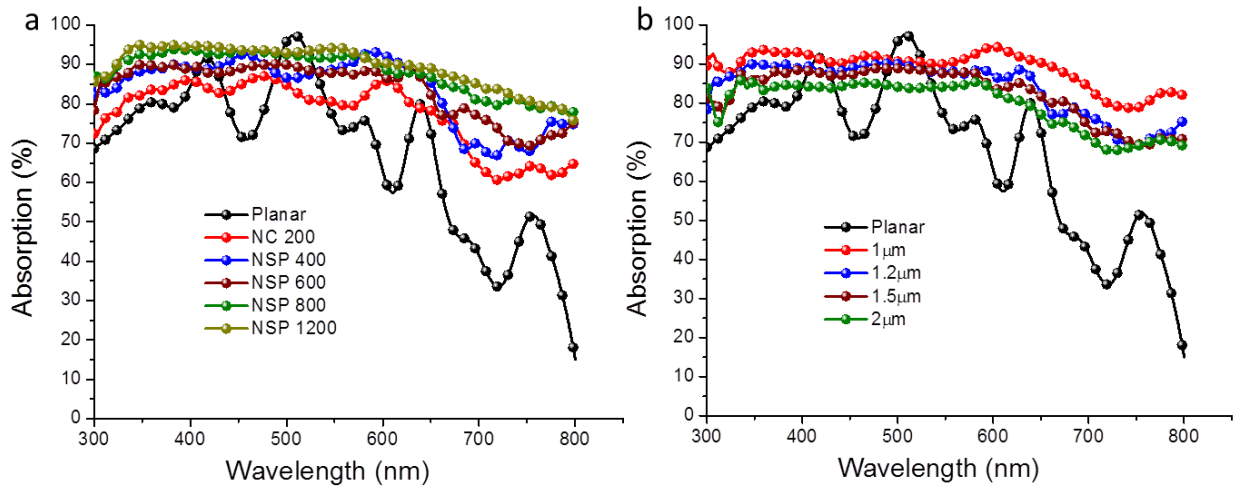## Optical absorption measurement

Figure S8: Optical absorption of solar cells with (a) different NSP heights of 1200 nm pitch and (b) device with best absorption within different pitches.
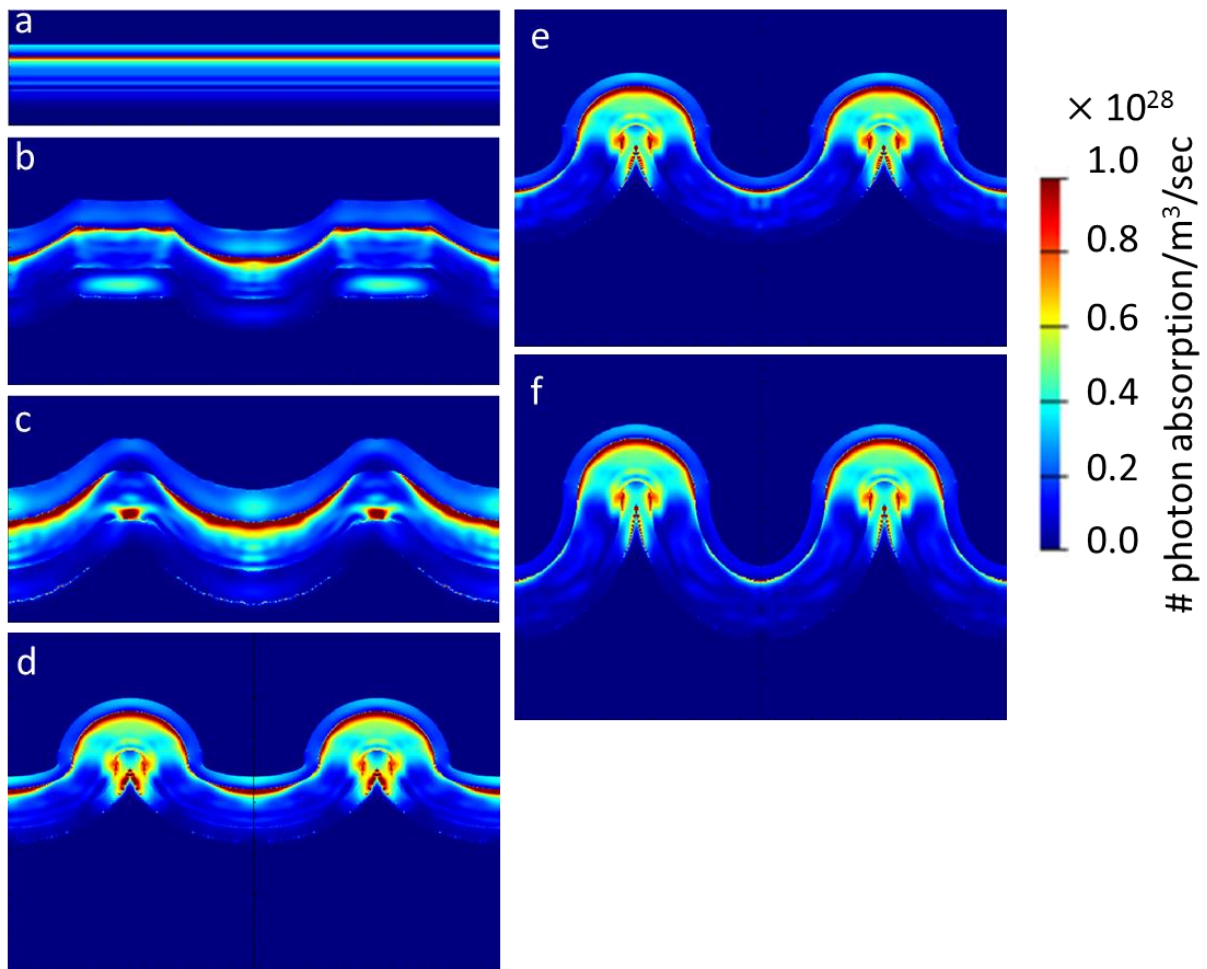
FDTD Simulation

Figure S9: Photon absorption rate profiles for 300-800nm broadband illumination of different structures: (a) planar, (b) NC 200, (c) NSP 400, (d) NSP 600, (e) NSP 800 and (f) NSP 1000. Note that profiles here are two simulation volumes wide and periodic boundary condition is imposed at the vertical boundaries.
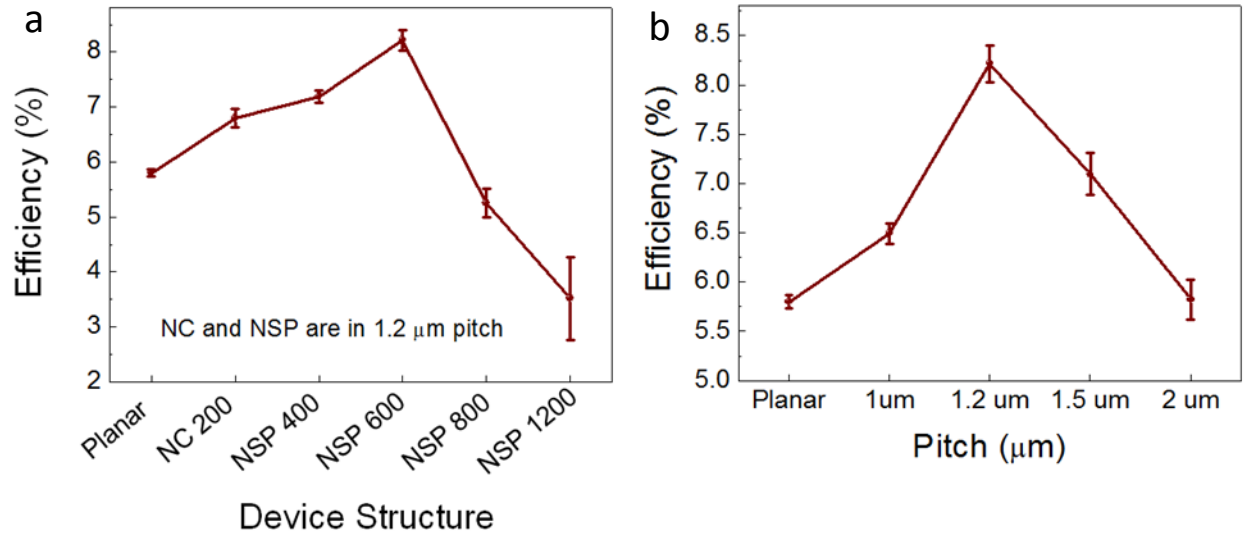
Figure S10: Solar cell efficiency statistics on (a) different morphologies NSP of 1200 nm pitch and (b) optimal NSP height in different pitches.

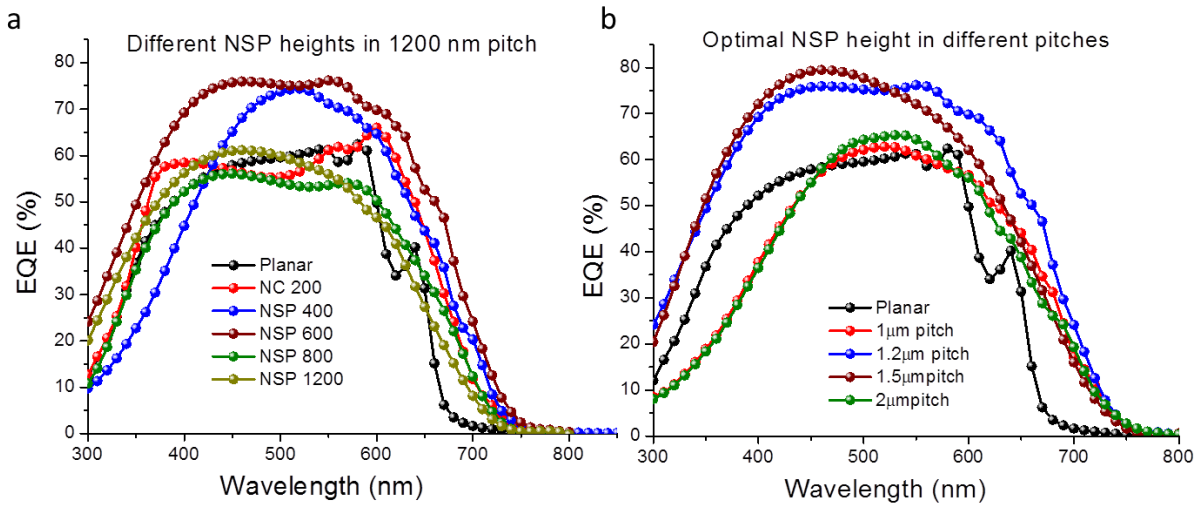# External quantum efficiency (EQE) measurement

Figure S11: EQE of best performance solar cell within (a) different morphologies NSP of 1200 nm pitch and (b) devices with optimal height in different pitches.
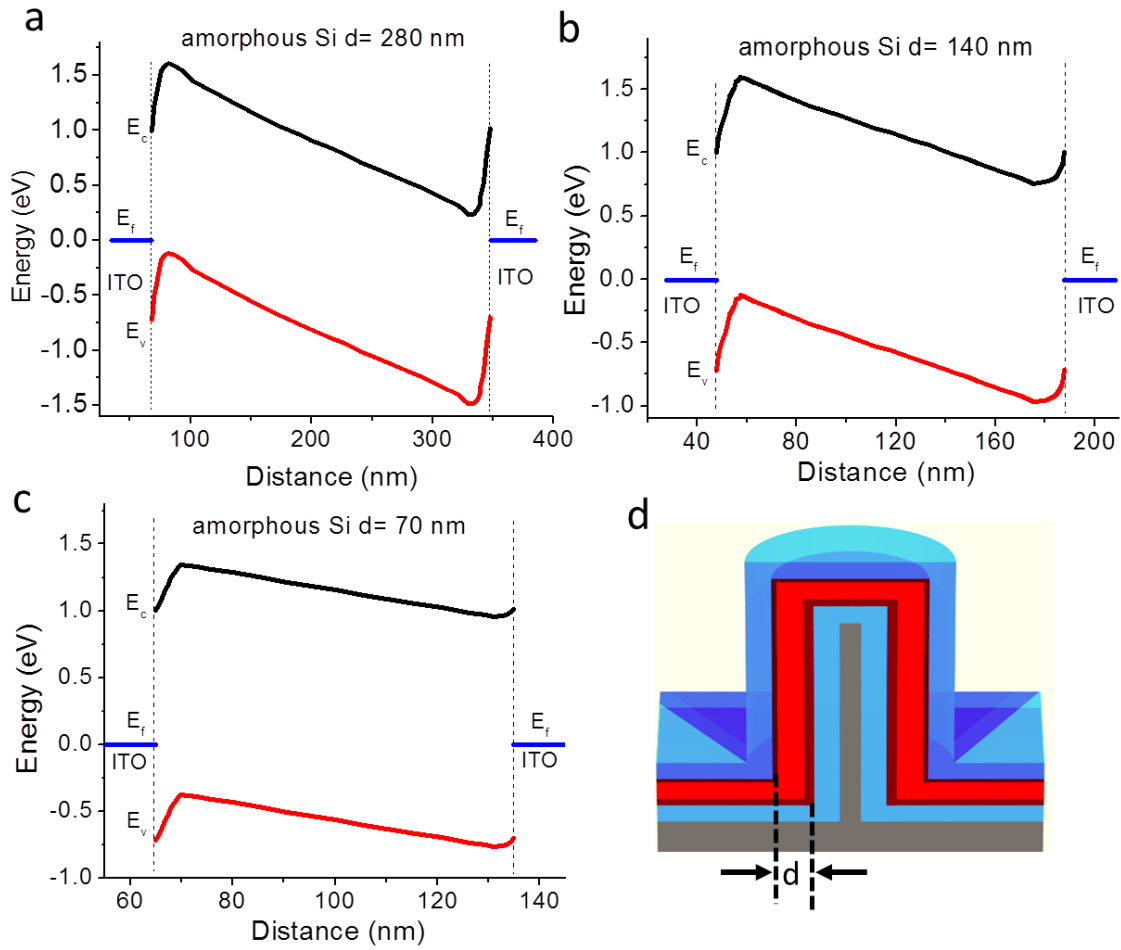
Device physics simulation

Figure S12: Calculated band bending diagram for different sidewall a-Si thickness (a) 280 nm (b) 140 nm , (c) 70 nm . (d) Schematic of cutting condition
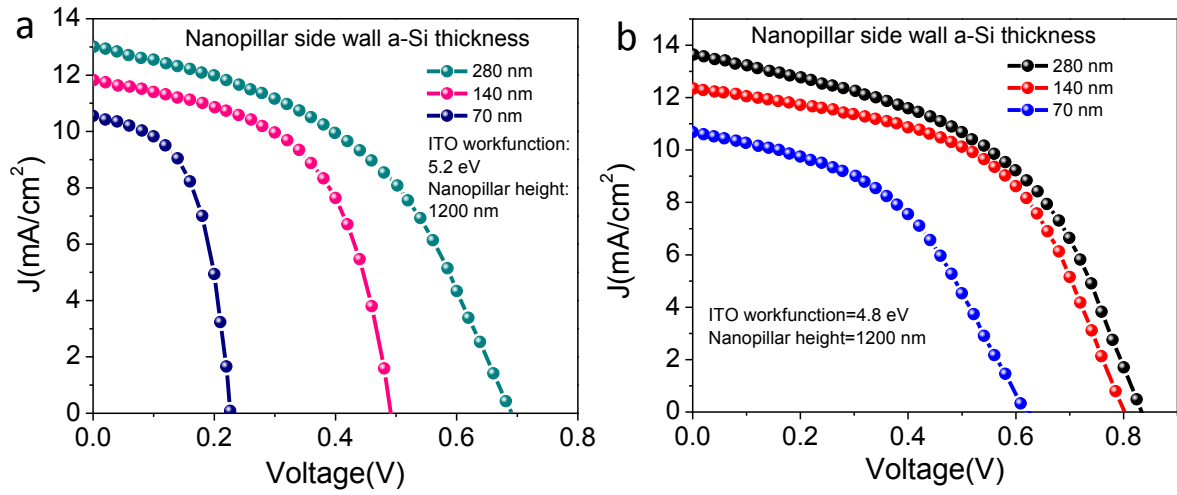
Figure S13: Simulated J-V curves of the nanopillar a-Si solar cells of different side wall

thicknesses with ITO workfunction of (a) 5.2 eV and (b) 4.8 eV.

Table S1: Anodization conditions for NSPs

Pitch (nm)	Electrolyte	Voltage (V)	Temperature (°C)	1st anodzation time (hours)
1000	1:1 (v:v) 4wt% Citric acid : Ethylene Glycol + 2.5mL 1wt% Phosphoric acid	400	10	3
1200	1:1 (v:v) 2wt% Citric acid : Ethylene Glycol + 9mL 0.1wt% Phosphoric acid	480	10	NSP 1200: 6 NSP 800: 4 NSP 600:3 NSP 400: 0.5
1200 (NC 200)	1:1 (v:v) 2wt% Citric acid : Ethylene Glycol + 9mL 0.1wt% Phosphoric acid	240	10	0.5
1500	1:1 (v:v) 1wt% Citric acid : Ethylene Glycol + 4mL 0.1wt% Phosphoric acid	600	5	16

2000	1:1 (v:v) 0.1wt% Citric acid : Ethylene Glycol	750	2	16

Table S2: Electrical parameters for Device Simulation (Silvaco Atlas)

Material parameters		Trap states		
Full thickness (p/i/n, nm)	20/240/20	Band tail states (exponential distribution)	Density of band tail states at conduction and valence band edge (cm^{-3})	2e20/2e20
Bandgap(eV)	1.72		Band tail Characteristic energy (conduction / valence band edge, meV)	30/50
Doping level (p/i/n, cm^{-3})	5e18/1e15/5e18		Capture cross section: (acceptor like/donor like trap states, cm^2)	Hole: 1e-15/1e-17 Electron:1e-17/1e-15
		Deep states(Gaussian distribution)	Total density states (acceptor like/donor like trap states, cm^{-3})	p,n: 5e16 i:5e15
Density of States (conduction band/ valence band, cm^{-3})	1e20/1e20		Peak position (eV) (acceptor like/donor like trap states, eV)	0.5Eg±0.5

			Characteristic decay energy(eV)	0.23
Mobility (electron/hole, $cm^2V^{-1}S^{-1}$)	1/0.03		Capture cross section (acceptor like/donor like trap states, cm^{-3})	Hole: 2e-14/8e-15 Electron: 2.7e-15/1.3e-14
Carrier life time (electron/hole, nS)	20/20			
ITO Work function(eV)	5			
Surface recombination velocity at ITO/a-Si interface (cmS^{-1})	Elecreon:1e7, Hole:1e7			