Electronic Supplementary Material (ESI) for Soft Matter.

Durability of Submerged Hydrophobic Surfaces

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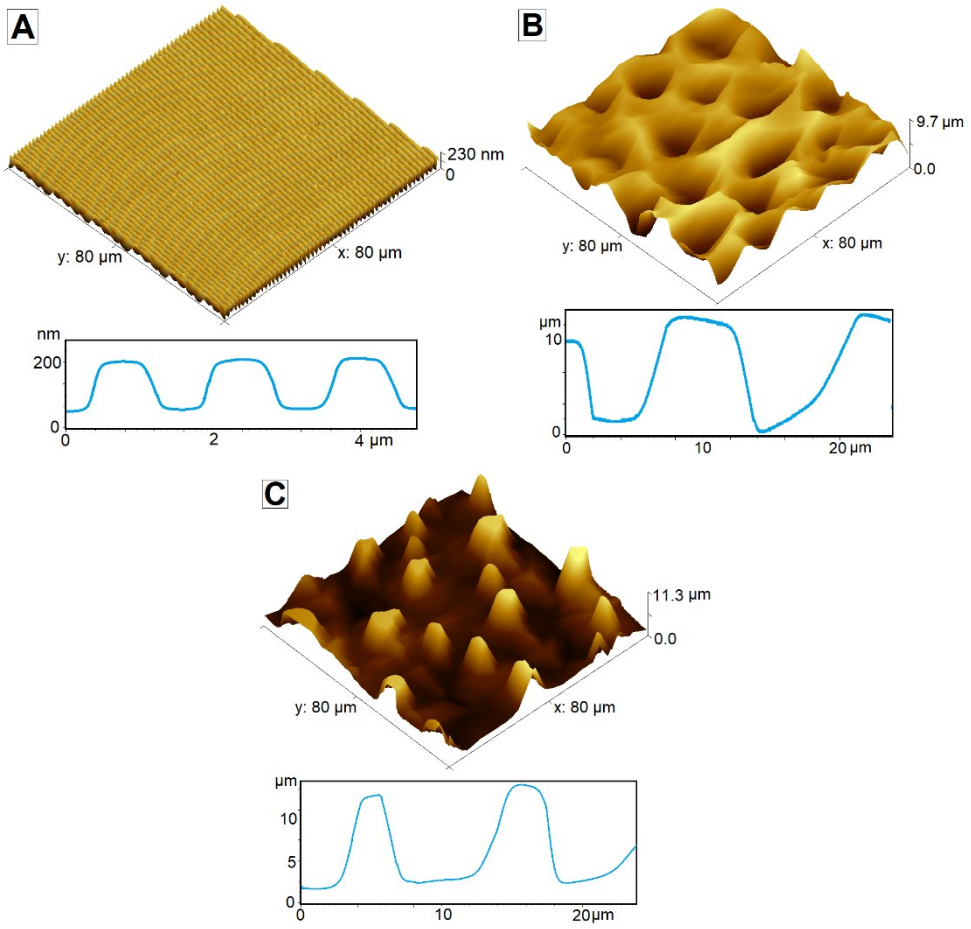

Fig. S1 *AFM images of the patterned Sylgard 184 samples along with cross sectional profiles. (A) Grating patterned sample with feature height (h_p) = 230 nm and periodicity (λ_p) = 1.5 µm. (B) Biomimetic negative replica of lotus leaf with average hole depth (h_D) = 9.7 µm and* average hole diameter (d_H) = 5.9 µm. *(C) Biomimetic positive replica of lotus leaf with average pillar height (h_P) = 11.3 µm and average pillar diameter (d_P) = 4.2 µm.*

In Wenzel state of wetting, the liquid is completely in contact with the surface and fully wets it. The apparent contact angle in Wenzel state, θ_W^* is given as:

$$\cos \theta_W^* = r \cos \theta_E \quad \text{..... (1)}$$

where r (≥1) is the roughness factor, defined as the ratio of the true area of surface to its projected area for the solid-liquid contact area at the top of the microstructures and θ_E is the intrinsic equilibrium contact angle of liquid on a smooth flat surface of the same material.

The apparent contact angle in Cassie state, θ_{CB}^* is given as:

$$\cos\theta_{CB}^* = r_f f \cos\theta_E - (1-f) \quad \ldots\ldots\ldots (2)$$

Here the r_f is the roughness factor of the wet surface area and f is the fraction of solid surface area wet by the liquid.

Table S1: *Comparison between experimental and calculated values of θ assuming Wenzel and Cassie state of wetting.*

Type of patterned surface	Roughness factor, r	Measured water contact angle, θ	Calculated θ_W^*	Calculated θ_{CB}^*	f	r_f
Grating substrate	1.31 ($< r_c$)	106.9± 1.1°	110.5°	132.5°	0.38	0.5
Negative replica of lotus leaf	3.8 ($> r_c$)	127.3± 2.8°	*	153.3°	0.12	0.41
Positive replica of lotus leaf	4.3 ($> r_c$)	151.5± 2.4°	*	160.7°	0.06	0.25

* As $r > r_c$, it is not possible to calculate θ_W^* as the value of cosθ comes out lesser than – 1.

In Table S1, the measured water contact angles (θ) and r values are given along with the theoretically calculated values for the Wenzel and Cassie-Baxter states as given by equations (1) and (2). The values of f and r_f were calculated assuming that the surface exhibits perfect Cassie state of wetting with entrapped air pockets. For a flat crosslinked PDMS surface, θ_E = 105.5°. The corresponding value of critical roughness factor, r_c = 3.74. The θ for a grating patterned was observed to be much closer to the value given by the Wenzel state and $r < r_c$. This confirms that grating patterned surfaces exhibits the Wenzel state of wetting. For the biomimetic negative and positive replicas of lotus leaf, as $r > r_c$, Wenzel state is not possible. For the negative replica, the θ is much lower than that predicted by Cassie-Baxter equation. This suggests that the surface can be in an intermediate state of wetting. The positive replica

of lotus leaf exhibits $\boldsymbol{\theta}$ closer to the value predicted by the Cassie state of wetting as given in table S1. Therefore, we can assume that the positive replicas show Cassie state of wetting.

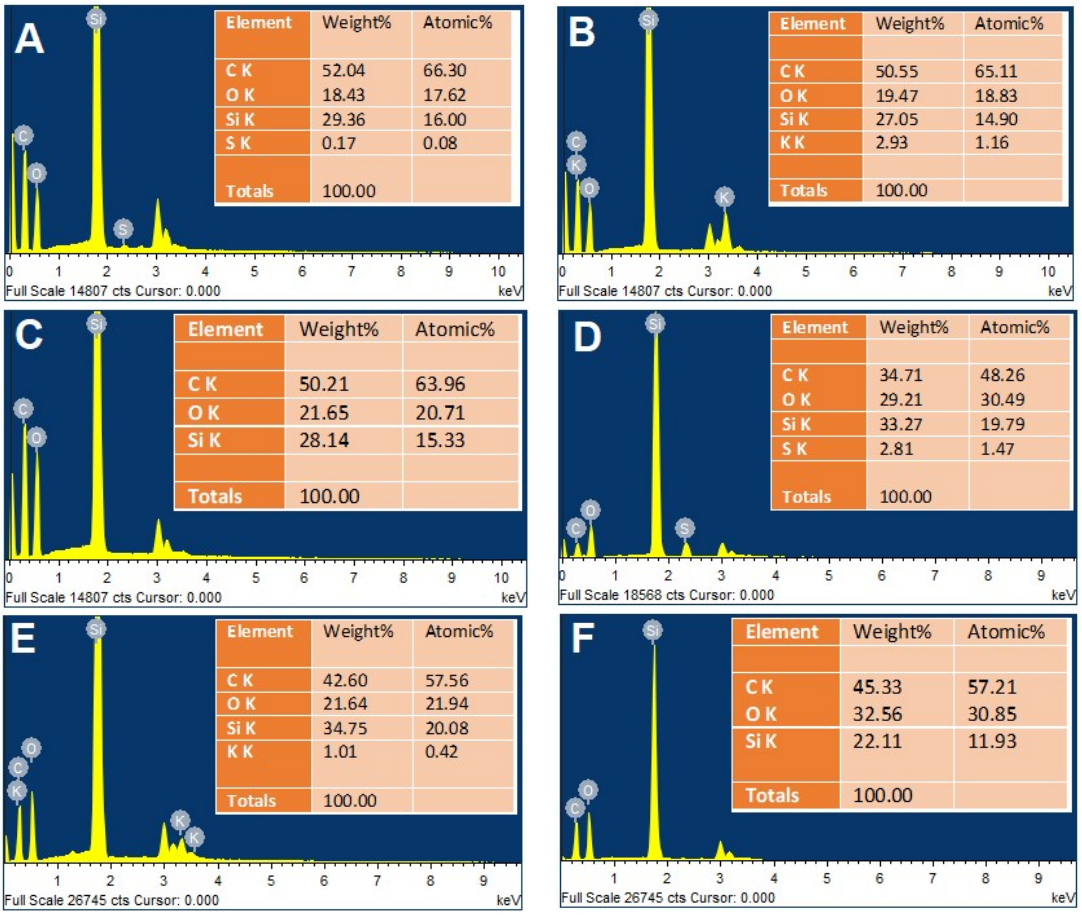

Fig. S2 *EDS analysis of negative and positive replicas of lotus leaf. Negative replicas immersed in (A) acidic, (B) basic, and (C) neutral solutions. The corresponding SEM images are shown as insets B1, D1 and F1 respectively in Fig. 4 of the main article. Positive replica of lotus leaf immersed in (D) acidic, (E) basic and (F) neutral mediums. The corresponding SEM images are shown as insets B1, D1 and F1 respectively in Fig. 5 of the main article.*

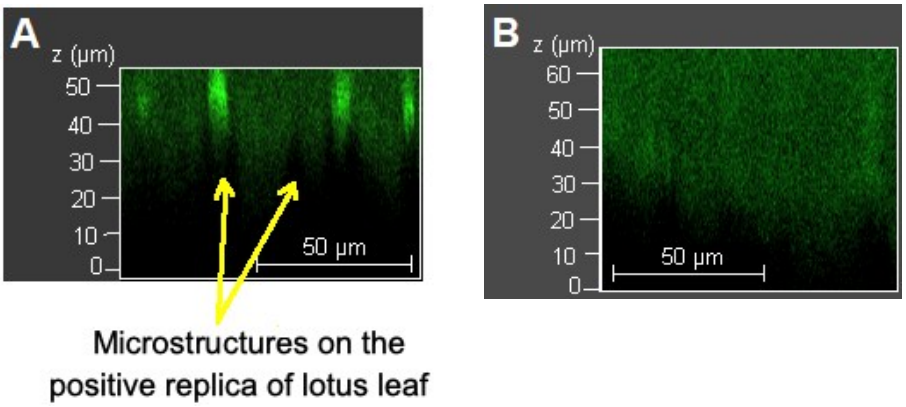

Fig. S3 *Confocal microscopy cross section image of biomimetic positive replica of lotus leaf immersed under water containing Rhodamine B dye: (A) After 10 mins of immersion showing partially penetration of the liquid meniscus and entrapped air pockets, and (B) at same position after 1 hr of immersion. The images show that the water penetrates gradually in between the surface asperities.*

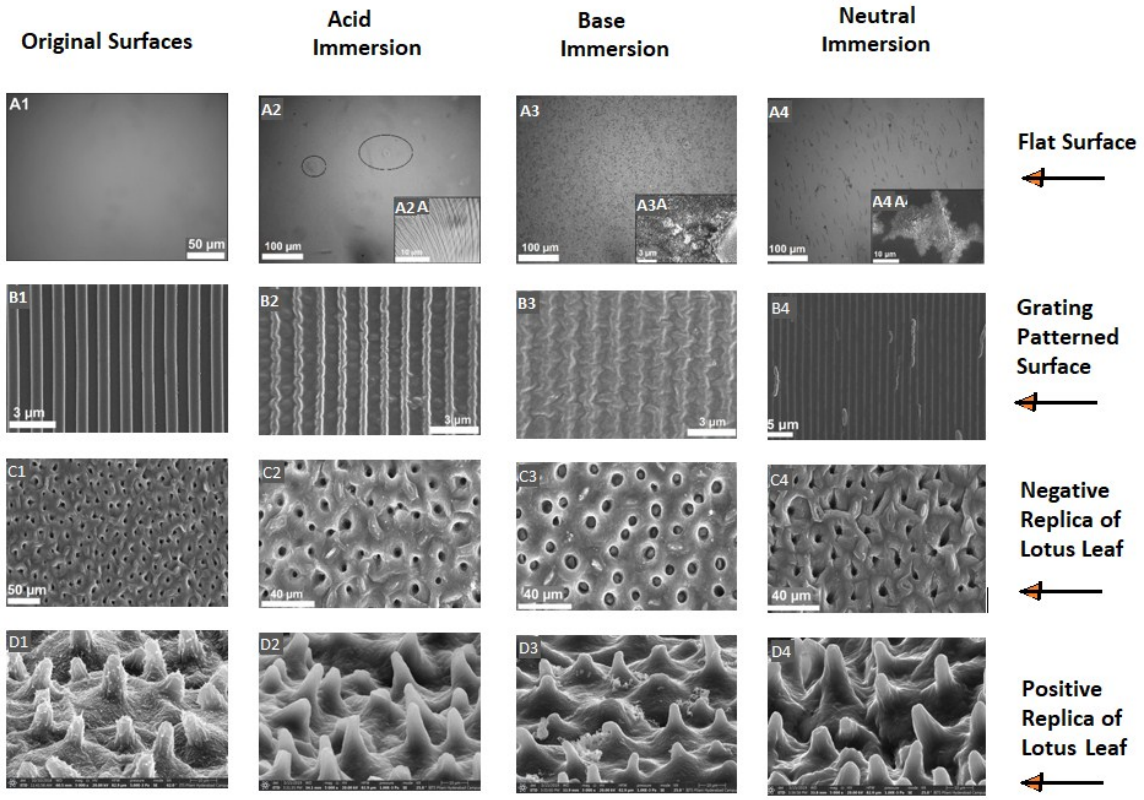

Fig. S4. *Composite of microscope images after* t_I *= 31 days. Each column represents the type of immersion medium and each row represents the type of the surface which are marked in the figure.*

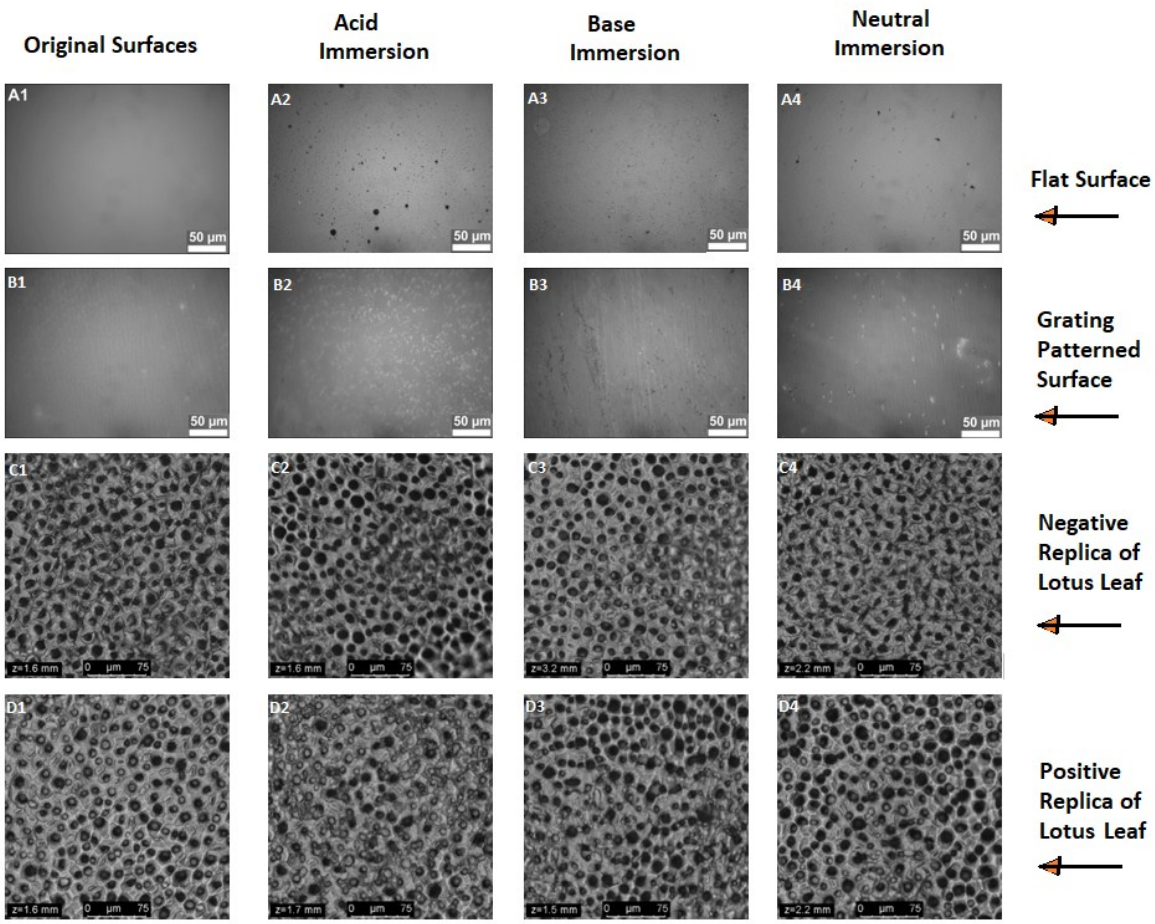

Fig. S5. *Composite of microscope images after* t_I *= 7 days. Each column represents the type of immersion medium and each row represents the type of the surface which are marked in the figure.*

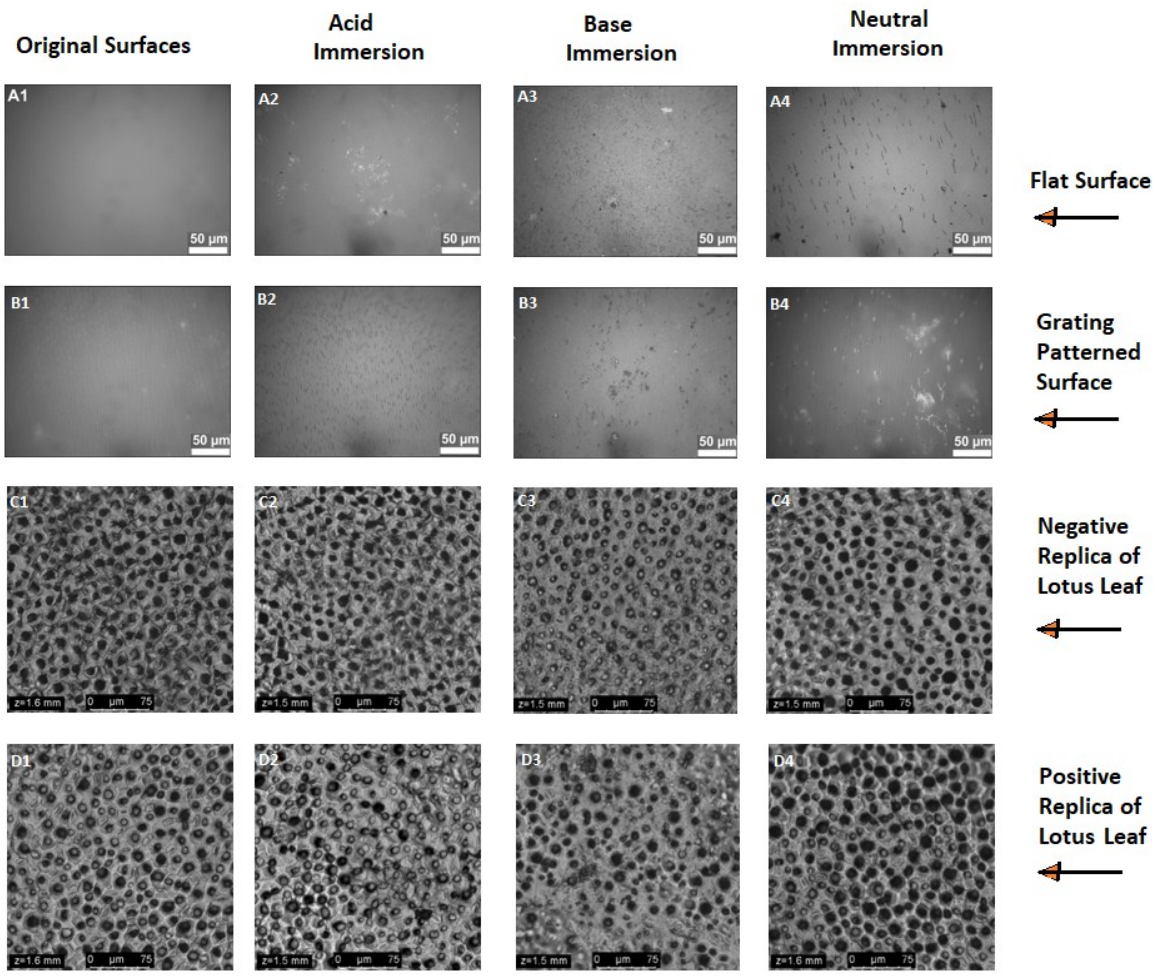

Fig. S6. *Composite of microscope images after* t_I *= 18 days. Each column represents the type of immersion medium and each row represents the type of the surface which are marked in the figure.*

Table S2: *Water contact angle(θ) for flat blocks of PDMS after immersion for different durations.*

Number of days immersed	Nature of immersion medium (θ in degrees)		
	Acidic	Basic	Neutral
0	105.08 ± 1.3	105.08 ± 1.3	105.08 ± 1.3
2	103.55 ± 1.8	104.10 ± 1.9	104.54 ± 1.2
4	99.98 ± 2.7	99.40 ± 2.1	103.56 ± 1.1
7	96.84± 1.8	94.15 ± 1.6	103.03± 3.2
11	95.78 ± 1.3	88.31± 1.8	102.67 ± 2.7
14	94.89± 2.1	75.51 ± 2.4	102.25 ± 2.1
18	93.15 ± 0.8	72.34± 2.5	101.99 ± 3.8
21	92.89 ± 2.9	71.35 ± 1.2	100.28 ± 1.1
25	92.17 ± 2.6	68.50 ± 2.0	99.52 ± 1.4
27	91.93 ± 1.8	68.07 ± 2.8	98.72 ± 0.7
31	91.68 ± 1.3	67.35± 1.1	97.91 ± 1.4

Table S3: *Water contact angle for grating patterned blocks of PDMS after immersion for different durations.*

Number of days immersed	Nature of immersion medium (θ in degrees)		
	Acidic	Basic	Neutral
0	106.88 ± 1.1	106.88± 1.1	106.88 ± 1.1
2	104.44± 1.1	84.95± 2.3	104.42± 1.7
4	97.96± 0.8	80.29± 1.1	102.65± 1.8
7	96.49± 1.5	75.09± 1.3	100.57± 1.2
11	93.30± 1.8	62.84± 1.8	99.86± 1.1
14	91.41± 2.3	60.90± 3.3	96.22 ± 2.5
18	91.33± 1.1	59.15± 1.3	91.89± 1.4
21	90.56± 1.9	56.81± 2.4	90.95± 2.4
25	90.01± 2.1	55.61± 2.1	90.21± 0.8
27	89.75± 1.9	50.75± 2.8	89.92± 2.1
31	89.09± 1.8	50.28± 3.2	89.67± 2.1

Table S4: *Water contact angle for biomimetic negative replicas of lotus leaf after immersion for different durations.*

Number of days immersed	Nature of immersion medium (θ in degrees)		
	Acidic	Basic	Neutral
0	127.30± 2.8	127.30± 2.8	127.30± 2.8
2	119.79± 3.3	108.50± 3.4	119.05± 3.2
4	108.8± 4.2	102.18± 2.3	112.74± 2.9
7	106.11± 4.0	101.92± 2.8	107.63± 1.8
11	104.84± 4.3	100.29± 3.1	106.62± 2.5
14	102.26± 3.8	92.03± 3.3	105.07± 2.8
18	100.62± 3.3	75.53± 2.3	101.86± 3.3
21	93.08± 4.4	75.04± 2.9	99.21± 3.0
25	92.71± 3.5	74.75± 2.9	98.43± 2.8
27	92.07± 3.3	65.98± 3.9	95.89± 2.1
31	91.89± 3.8	64.70± 1.3	93.94± 2.0

Table S5: *Water contact angle for biomimetic positive replicas of lotus leaf after immersion for different durations.*

Number of days immersed	Nature of immersion medium (θ in degrees)		
	Acidic	Basic	Neutral
0	151.54± 2.4	151.54± 2.4	151.54± 2.4
2	123.25± 2.9	128.14± 2.9	144.65± 4.3
4	121.46± 2.7	107.97	109.36± 3.2
7	106.39± 3.9	104.77± 2.9	108.74± 3.9
11	106.07± 3.1	102.29	108.09± 2.9
14	105.84± 2.8	100.24	107.61± 3.2
18	104.64± 3.7	97.50± 3.9	105.95± 2.6
21	103.09± 2.5	97.37± 2.4	103.35± 2.7
25	102.28± 3.9	96.57± 4.3	102.89± 3.6
27	101.41± 2.1	95.72± 2.9	102.05± 3.7
31	100.31± 4.2	95.19± 2.7	101.05± 3.9