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Nonsolvent-assisted Fabrication of the StructurizedPloylactideas Superhydrophobic Surfaces

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1. Materials

Polylactide (PLA) resin (4032D) was a semicrystalline grade one in the form of pellets and commercially supplied by NatureWorks Co. Ltd (Minnetonka, USA). Chloroform, dichloromethane, absolute ethyl alcohol, n-butyl alcohol, and n-butyl acetate were purchased from Tianjin Chemical Regent Co., Ltd. (China) and used as received.

2. Preparation of PLA-i, PLA-ii, PLA-iii, PLA-iv and PLA-v coatings

Table 1 shows the solvent and nonsolvent used to prepare PLA-i, PLA-ii, PLA-iii, PLA-iv, and PLA-v samples. In the case of sample PLA-i, a known amounts of dried PLA (2.34g) pellets were dissolved in a given solvent/nonsolvent mixture at room temperature under magnetic stirring. The weight ratio of chloroform (solvent) to PLA was fixed at 2:1 (w/w) and the weight ratio of PLA to absolute ethyl alcohol (nonsolvent) was varied between 0-5 wt% with a step increment of 0.5 wt%. According to the same procedure, PLA-ii coating was fabricated using chloroform as a solvent and absolute ethyl alcohol/n-butyl alcohol as a binary non-solvent. The ratio of absolute ethyl alcohol to n-butyl alcohol was kept at 1:1. PLA-iii coating was fabricated using DCM as solvent and absolute ethyl alcohol as non-solvent; and PLA-iv coating was fabricated by using (DCM) as solvent, n-butyl alcohol and n-butyl acetate as binary non-solvent with the rate of n-butyl alcohol and n-butyl acetate kept as 1:1; likewise, PLA-v coating was fabricated by using DCM as solvent, absolute ethyl alcohol, n-butyl alcohol and n-butyl acetate as ternary non-solvent with the rate of absolute ethyl alcohol, n-butyl alcohol and n-butyl acetate kept as 1:1:1.

3. Characterization

The morphologies of the film surfaces were observed using scanning electron microscopy (SEM, JEOL, JSM-7500F, Japan) at an accelerating voltage of 5kV and atomic force microscopy (AFM, Shimadzu Corp.，SPM-9500J3，Japan) operated in a tapping mode, respectively. Differential scanning calorimetry (DSC) measurements were performed using a PerkinElmer Pyris Diamond DSC under a nitrogen atmosphere at the heating rate of 10℃/min from home temperature to 200℃. The weight of DSC sample was about 3-5mg. Water contact angleS of the film on the glass slide was measured with a Contact angle analyzer (Powereach, JC2000A, China) based on a sessile drop measuring method at ambient temperature. The volume of DI water droplet was 4μL and five different points for each film were tested. The contact angle hysteresis (CAH) on the sample was measured at the room temperature with CA System (DSA100, Kruss Co., Germany). The adhesion force was assessed by a highly sensitive microelectromechanical balance system (Kruess). A 10μL ultrapure Milli-Q water droplet with an electrical resistivity of $10^{18}\Omega\cdot cm$ was suspended on a home-built platinum semispherical cap, which was mounted o the microelectromechanical balance system.

Table S1. Thermal and wettability parameters of the samples (prepared with a lid) with varying contents of nonsolvent

Sample	Nonsolvent content/mL	CA/°	ϑa/°	ϑr/°	$(\vartheta a-\vartheta r)$/°	T_m/℃	ΔH_f/J·g-1	X_c/%
PLA-i	0.5	82	-	-	-	162.3	18.71	20.10
PLA-i	3	151	151.1	138.9	12.2	162.4	62.17	66.78
PLA- ii	2.5	90	-	-	-	162.4	32.25	34.64
PLA- ii	3.5	150	151	137	14	162.0	55.03	59.11
PLA- iii	0.5	88	-	-	-	162.1	21.65	20.09
PLA- iii	1.5	140.3	-	-		162.4	33.82	36.33
PLA- iv	1	88.3	-	-	-	161.7	48.49	52.08
PLA- iv	3.5	151.3	151.5	135.4	16.1	163.9	57.29	61.54
PLA- v	2	95.3	-	-	-	162.4	33.92	36.43
PLA- v	3	151.8	152.1	139.5	12.6	159.9	51.07	54.83

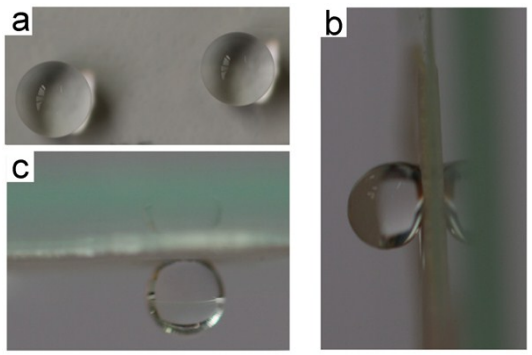

Fig.S2 Images of water droplets of 4 µL on the PLA-v surface with different tilt angles: (a) 0°, (b) 90°, and (c) 180°.