Supporting information for

Tanning agent free leather making enabled by the dispersity of collagen fibers combined with superhydrophobic coating

Xiu He,[a] Yawen Huang,[a] Hanzhong Xiao,[a,b] Xiuzhen Xu,[a] Yujia Wang,[a,b] Xin Huang,[a,b] * Bi Shi[a,b]*

[a]National Engineering Research Center of Clean Technology in Leather Industry, Sichuan University, Chengdu China, 610065.

[b]Department of Biomass Chemistry and Engineering, Sichuan University, Chengdu China, 610065.

[*]Corresponding author: xhuangscu@163.com (X. Huang), sibitannin@vip.163.com (B. Shi)

Experiments

Materials

Pickled pelt, using as raw material, was supplied by Ruixing Leather Co., Ltd (Haining, China). Sodium bicarbonate, ethanol, tetrabutyl titanate, N, N-dimethylformamide (DMF) were of analytical grade and used without further purification. Polydimethylsiloxane prepolymer (Sylgard 184A) and curing agent (Sylgard 184B) were purchased from Dow Corning Corporation (Midland, USA). Hydrophobic SiO_2 nanoparticles with the average particle size of 10-15 nm were purchased from Henan Nano Materials Engineering Technology Research Center (Henan, China). Polyurethane was purchased from Dongtai Polymer Materials Co., Ltd (Fujian, China). Chrome powder (24% Cr_2O_3, 33% basicity) was provided by Minfeng Chemical Co., Ltd. (Chongqing, China). Commercial fatliquors were used as received, including PROVOL BA, PELGRASSOL MB (Zschimmer Schwarz GmbH & Co KG Chemische Fabriken, Koblenz, Germany) and DOWELLOR FS-90 (Dowell Science and Technology Co., Ltd., Chengdu, China).

Preparation of dehydrated pelts and tanning agent free leather

Pickled pelt cut from the back region was used for fabricating dehydrated pelt. Before the dehydration, the pickled pelt was treated by desalinization. In brief, water (200 wt%, based on the weight of pickled pelt, similarly hereinafter) and NaCl (14 wt%) were added into the drum, followed by rotation for 10 min. Then, the pH of liquor was increased to 5.8. After that, the drum kept rotating for 4.0 h and then stood overnight. Subsequently, the drum rotated for 30 min, and then, the liquor was discharged. The resultant pelt was treated by 4 times of washing with water (800 wt%). For each washing, the washing time was 20 min. After squeezing the water of

desalted pelt, dehydration with ethanol was carried out. 150% ethanol was added into the drum to dehydrate the desalted pelt. After rotating for 120 min, the float was discharged. A total of 6 times of dehydration with ethanol was carried out.

The dehydrated pelt was used for preparation of tanning agent free leather. The dehydrated pelt with water content of 4.65% was added in ethanol solution containing tetrabutyl titanate (0.6 mol/L), followed by rotating for 30 min at room temperature, and then dried at 60 ℃. Subsequently, the resultant intermediate was immersed into PDMS solution (50 g/L) for 5.0 min, and then dried at 60 ℃. In this way, the tanning agent free leather was prepared. The PDMS solution (50 g/L) was prepared as following: Sylgard 184A (4.54 g) and Sylgard 184B (0.45 g) were dissolved in 50 mL of dodecane, respectively. The two solutions were then mixed together by magnetic stirring.

Besides the above PDMS coating, the dehydrated pelt can also become superhydrophobic via spray-coated polyurethane and hydrophobic SiO_2 nanoparticles. Specifically, DMF dispersion containing 0.8 wt.% of polyurethane and 1.52 wt.% of hydrophobic SiO_2 nanoparticle was ultrasonically for 1.0 h, and then spray-coated onto the dehydrated pelt at the pressure of 0.4 MPa, followed by drying at 60°C.

For comparison, chrome tanned leather was prepared by using the pickled pelt cut from the back region. Briefly, water (200 wt%, based on the weight of pickled pelt, the same below) and NaCl (14 wt%) were successively added into the drum, followed by rotating for 10 min at room temperature. Then, the pickled pelt and chrome powder (12 wt%) was added into the drum, followed by rotating for 180 min at room temperature. After that, the pH of tanning liquor was slowly increased to 3.8 and run for another 30 min at room temperature. Subsequently, 200% of water was added into the drum and the temperature of tanning liquor was increased to 40 ℃, followed by

rotation for 120 min and standing overnight. After rotating for 30 min in the next day, the resultant leather was taken out from the drum, which was then horsed up for 24 h. After that, the resultant leather and water (200 wt%, based on the weight of tanned leather, similarly hereinafter) were added into the drum. The pH of liquor was adjusted to 6.2, and then the drum was kept rotating for another 60 min at 35 ℃. Subsequently, commercial fatliquors (PROVOL BA 6.0 wt%, DOWELLOR FS-90 3.0 wt%, PELGRASSOL MB 1.0 wt%), were added into the drum. The temperature was kept at 50 ℃ for 60 min, and then the pH of liquor was decreased to 3.8, followed by washing with water (400%) for 10 min. After dried and softened, the chrome tanned leather was obtained.

Characterizations

Water content in pelt/dehydrated pelt was analyzed by Karl Fischer titration (V20S, METTLER, Switzerland). Pore structure of leather samples were analyzed on mercury intrusion porosimetry (AutoPore IV 9500, Micromeritics, USA). The microstructure of samples was observed using field emission scanning electron microscope (FESEM, Nova Nanosem 450, FEI, USA) at an accelerating voltage of 5 kV. The elemental composition of samples was obtained by energy dispersive X-ray spectroscopy (EDS, Azteclive Ultim Max 100, Oxford Instruments, UK). The element analysis on the surface of the samples was performed using X-ray photoelectron spectrum (XSAM800, Kratos, UK). The wetting properties of tanning agent free leather were measured on a contact angle goniometer (DSA30, Krüss GmbH, Germany). 5.0 μL of water droplet was dropped onto the surface of samples. Quantified surface roughness was measured by an optical profiler (Contour GT-K1, Bruker, USA). Leather samples were first conditioned at 20℃ and 65% relative

humidity for 48 h according to IUP 3 standard method to measure their physical properties. Tensile strength, tear strength and elongation at break of leather samples were obtained from a tensile tester (AI-7000SN, Gotech, China) according to IUP 6 and IUP 8 standard method, respectively. The fullness of leather samples was measured by compression performance. Thermal stability of leather samples was evaluated by determining the loss of area after heating at 150 ± 5℃ for 30 min in an oven.

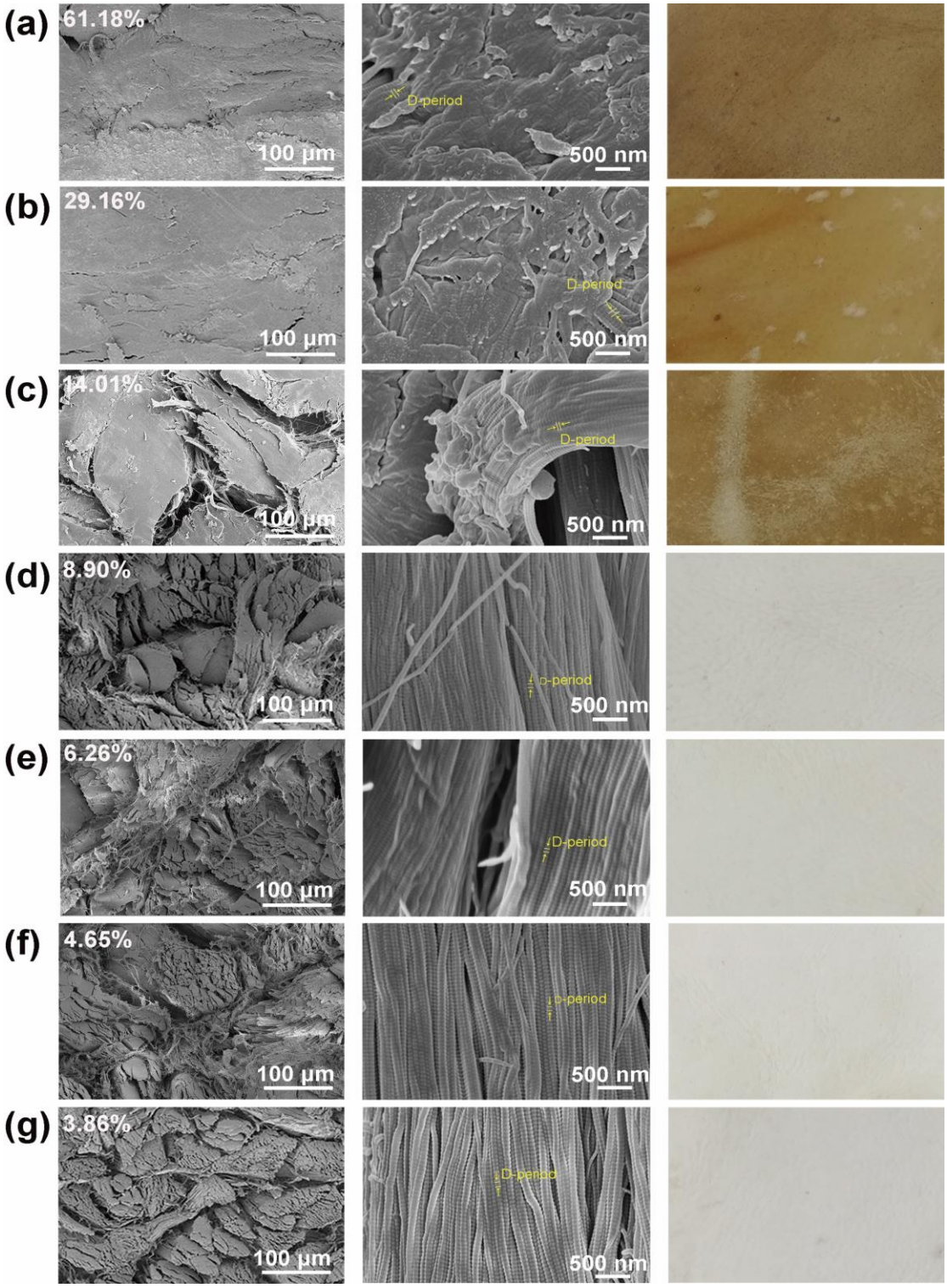

Fig. S1 FESEM images of pelts with different water contents at different magnifications and the corresponding optical photos of pelt surface, where the water content of pelts in (a), (b), (c), (d), (e), (f), (g) is 61.18%, 29.16%, 14.01%, 8.90%, 6.26%, 4.65% and 3.86%, respectively.

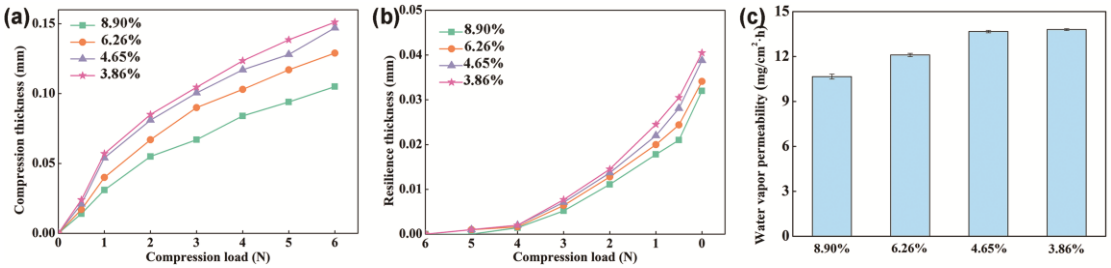

Fig. S2 Influences of water content on the compression performance (a), resilience performance (b), and water vapor permeability (c) of dehydrated pelts.

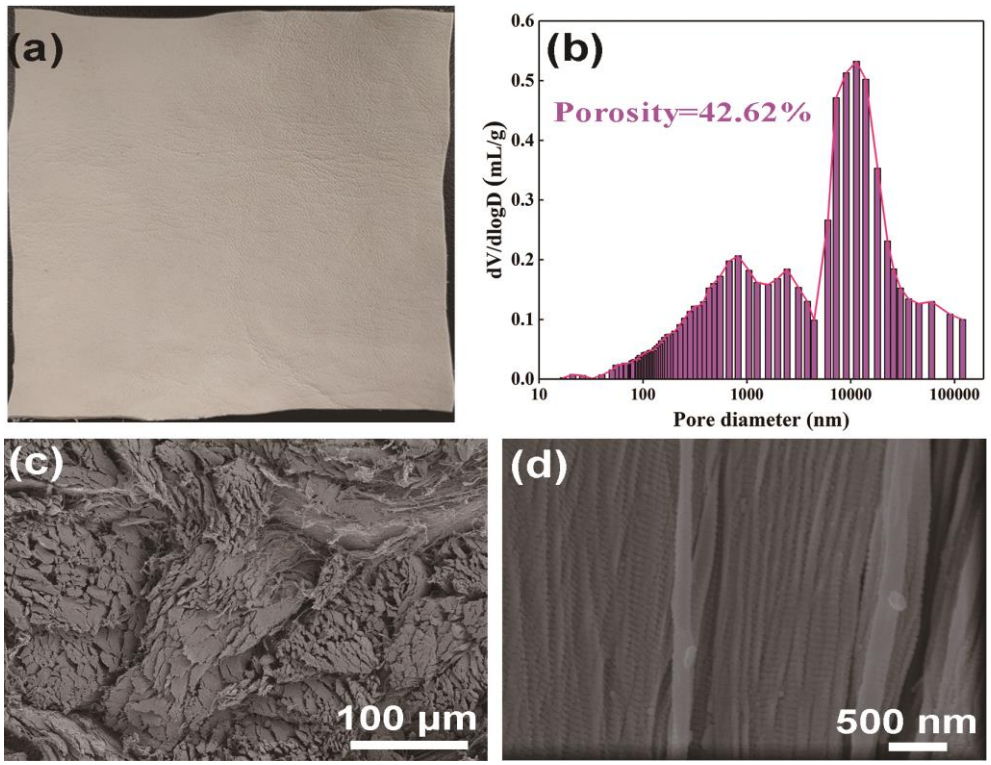

Fig. S3 The digital photo (a), pore size distribution (b) and FESEM images (c, d) of dehydrated pelt treated by one-step dehydration with 750% of ethanol.

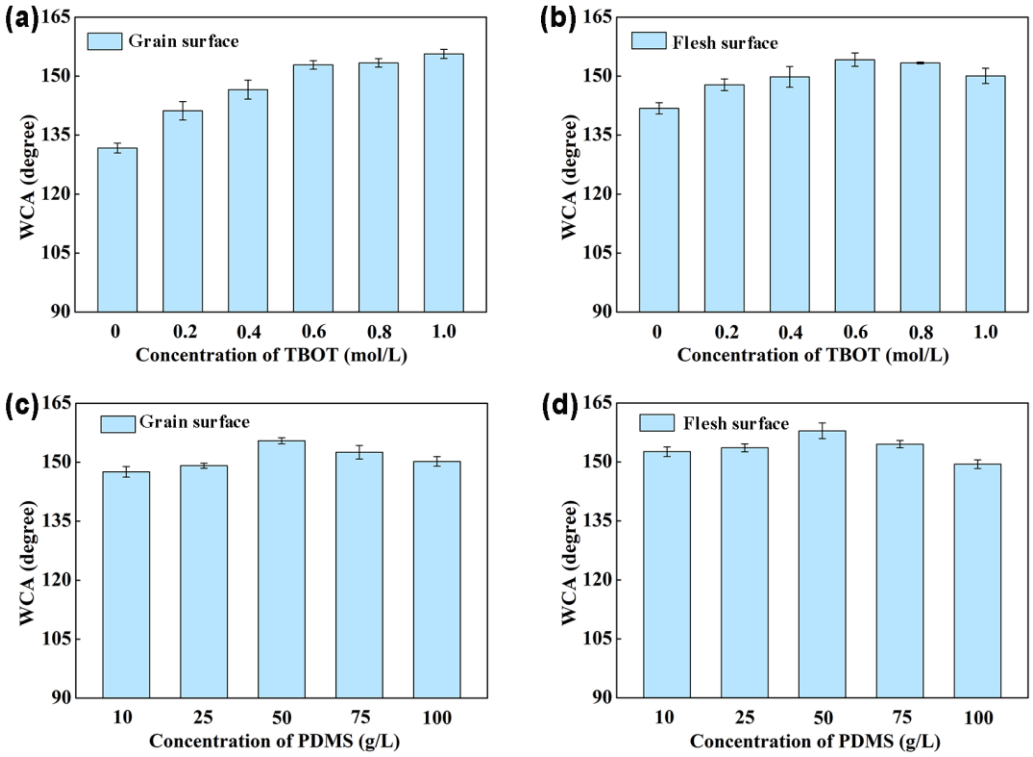

Fig. S4 The water contact angle at the grain surface (a, c) and flesh surface (b, d) of dehydration pelts that were prepared by different concentrations of TBOT and PDMS.

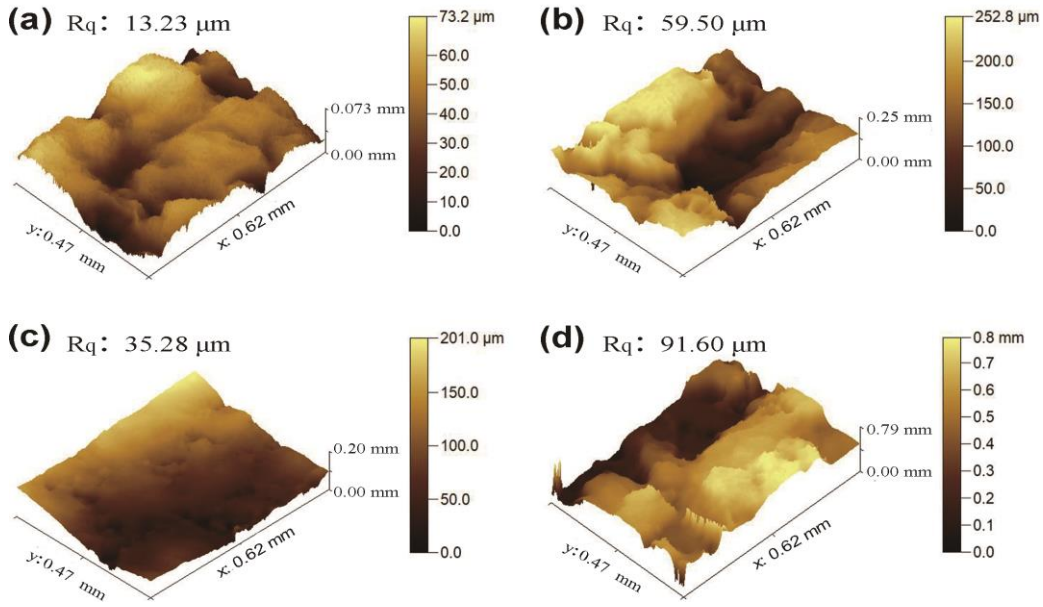

Fig. S5 Optical profile images showing the grain surface (a) and flesh surface (b) of dehydrated pelt, and the grain surface (c) and flesh surface (d) of dehydrated pelt treated by *in situ* growth of TiO_2NPs.

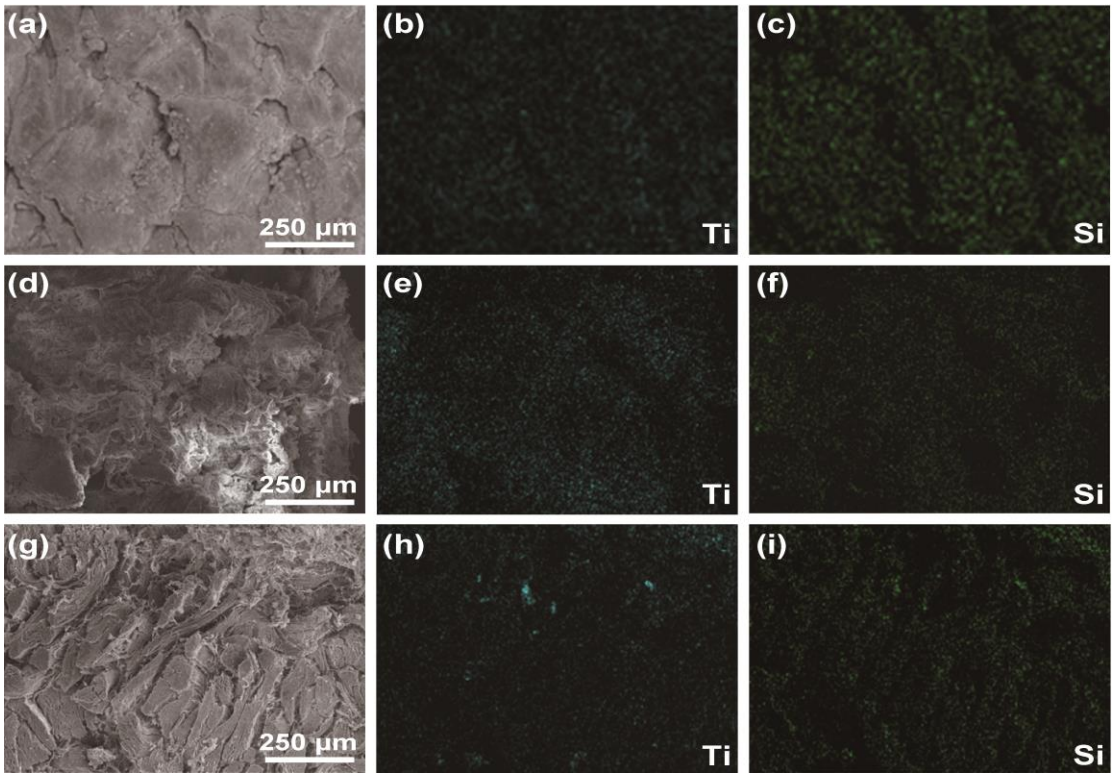

Fig. S6 FESEM images and EDS mapping images of the grain surface (a-c), flesh surface (d-f) and cross-section (g-i) of tanning agent free leather.

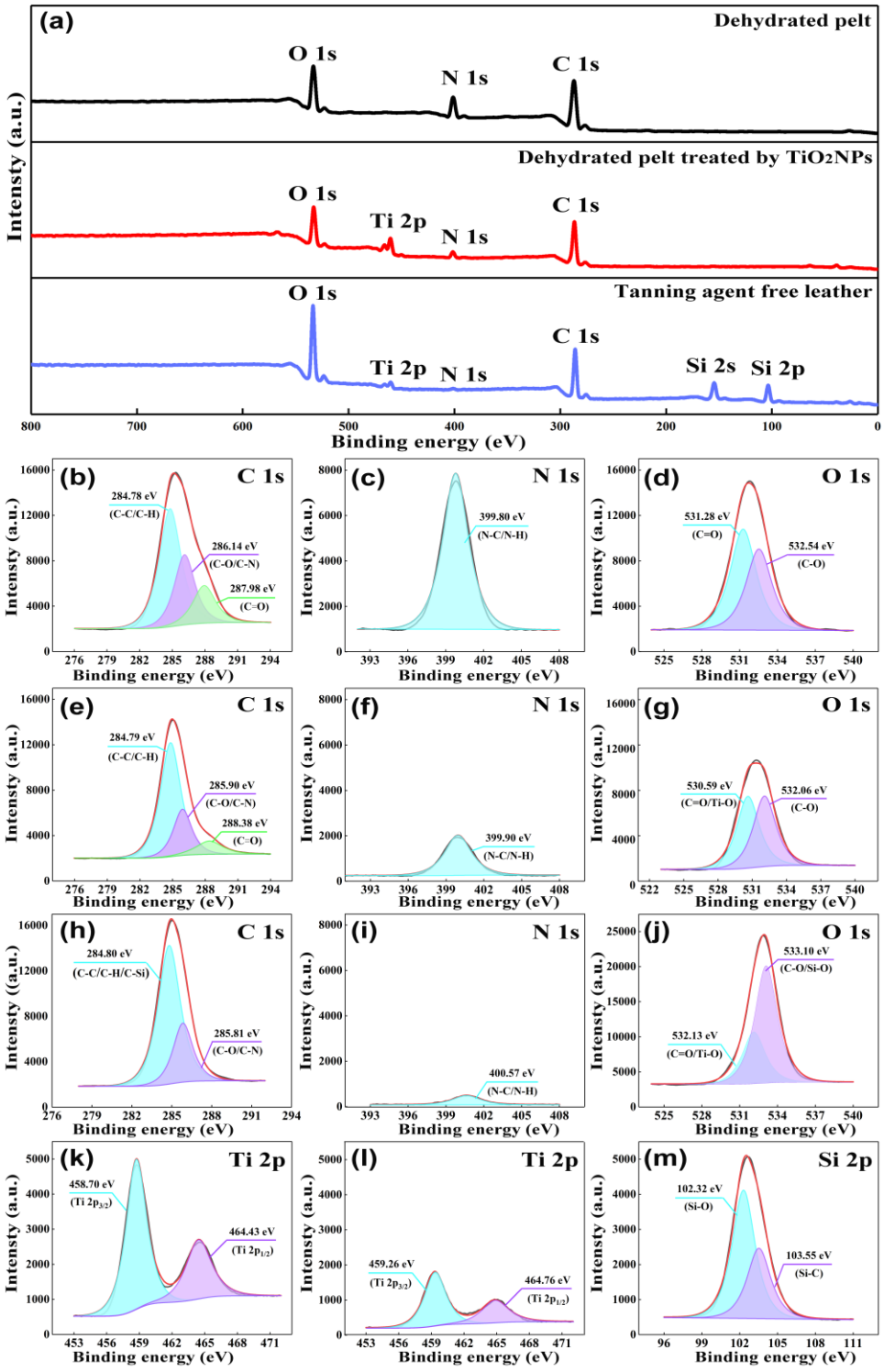

Fig. S7 XPS survey scans of dehydrated pelt, dehydrated pelt treated by TiO_2NPs and tanning agent free leather (a), C 1s (b), N 1s (c) and O 1s (d) spectra of dehydrated pelt, C 1s (e), N 1s (f), O 1s (g) and Ti 2p (k) spectra of dehydrated pelt treated by TiO_2NPs, C 1s (h), N 1s (i), O 1s (j), Ti 2p (l) and Si 2p (m) spectra of tanning agent free leather.

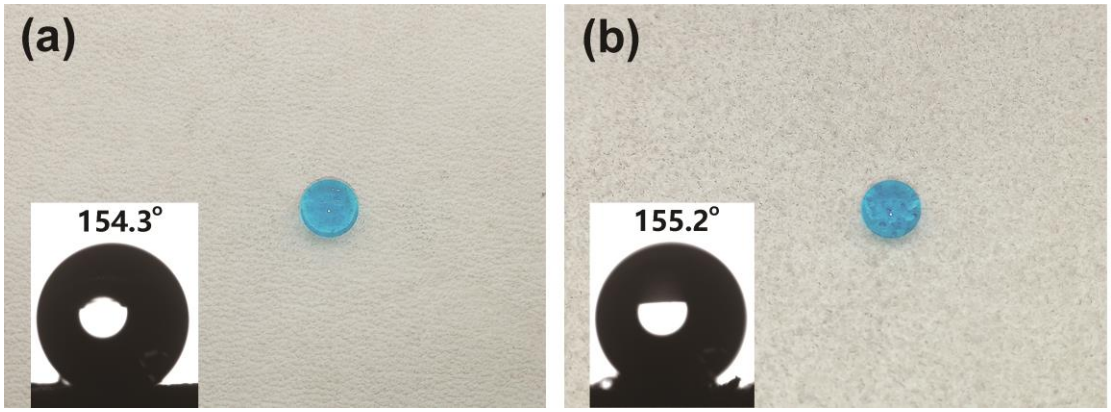

Fig. S8 The digital photos of water droplets (50 μL, colored by methyl blue) on the grain surface and flesh surface of tanning agent free leather that was prepared by spray-coated polyurethane and hydrophobic SiO_2 nanoparticles. Insets in (a) and (b) show the corresponding images of water contact angle at the grain surface (154.3°) and flesh surface (155.2°), respectively.