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# Self-driven directional dehydration enabled eco-friendly manufacture of chrome-free leather

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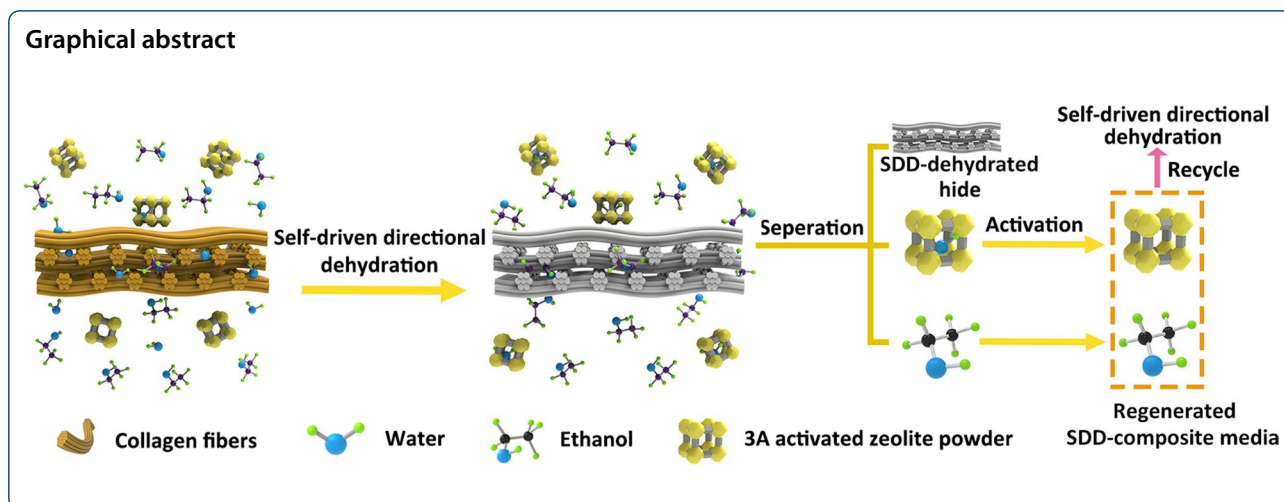
## Abstract

Manufacture of eco-friendly chrome-free leather is of great significance for realizing sustainable development of leather industry. Conventional tanning theory believes that it is impossible to convert raw hide to leather without the utilization of cross-linking agent (e.g., chrome salts) among collagen fibers in raw hide. Here, we developed a brand-new leather manufacture strategy that relied on the composite dehydration media enabled self-driven directional dehydration mechanism to accomplish chrome-free leather manufacture for the first time, rather than followed the classic cross-linking mechanism that has been obeyed for more than one century in leather industry. We demonstrated that the essence of leather making is to regulate the water content in raw hide rather than to form cross-linkage among collagen fibers. The composite dehydration media comprised of anhydrous ethanol and molecular sieves (3A activated zeolite powder) successfully guaranteed continuous self-driven directional dehydration of raw hide by establishing stable water concentration gradient between raw hide and ethanol, which significantly increased the dispersity of collagen fibers in raw hide (with the water content reduced from 56.07% to 5.20%), thus obtaining chrome-free leather that is more ecological than chrome-tanned leather due to the elimination of any tanning agent. The as-prepared chrome-free leather exhibited outstanding tear force (174.86 N), tensile strength (24.56 N mm<sup>-2</sup>), elongation at break (53.28%) and dry-thermal stability, superior to chrome-tanned leather. Notably, the used composite dehydration media was recyclable for chrome-free leather manufacture, therefore facilitating an environmentally benign leather manufacture process. Our investigations are expected to open up a new conceptual leather making strategy that is applicable for realizing substantial manufacture of eco-friendly leather.

**Keywords:** Chrome-free leather, Eco-friendly manufacture, Regulation of water content, Self-driven directional dehydration, Recyclability of dehydration media

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## 1 Introduction

Tanned animal hide, well known as leather, has been the most ancient wearable material, which is ubiquitously utilized in our daily life, from shoe to garment and furniture [1–4]. Based on the classic leather making theory that has been followed by more than one century, animal hide has to undergo a tanning process before converted to leather, which employs tanning agents to form cross-linkages among collagen fibers so as to endow the resultant leather with enhanced thermal stability and mechanical strength significantly [5–8]. Classic leather making theory believes that cross-linkage among collagen fibers is an indispensable necessity to convert raw hide to leather, and this theory has been widely accepted by the leather community [9, 10]. At present, tanning theory based on cross-linkage has dominated the leather science, and chrome-tanning is currently commercialized cross-linkage theory-based leather manufacturing technique [11, 12]. However, chrome pollution is always a persisting concerned environmental issue confronted by the leather industry [13–15], which has to be solved radically for realizing environmental benign and sustainable leather manufacture. To address this critical challenging issue in leather industry, great efforts have been dedicated to explore chrome-free tanning agents during the past several decades, including two major categorizes of non-chrome metal salts and organic tanning agents [16–18]. All these developed chrome-free tanning agents exclusively follow the classical tanning theory by forming cross-linkages among collagen fibers without the utilization of chrome. Nevertheless, all current chrome-free tanned leathers still fail to provide desired thermal stability and mechanical strength that are comparable to those of chrome-tanned leather [19, 20], and these chrome-free tanning process still involved the discharge of non-chrome metal and/or organic pollution [21, 22]. These

attempts of past several decades on non-chrome tanning promoted us to meditate on whether cross-linkage is a real necessity to accomplish the tanning of leather. If cross-linkage is not indispensable for the raw hide to convert to leather, a breakthrough of environmentally benign and sustainable leather manufacture is likely possible to achieve by a complete elimination of the use of tanning agent that is a necessity for a conventional cross-linking theory-based tanning process of leather making.

Normally, the water content in raw hide is 65%–75% while all the leathers exhibit a considerable decrease of water content after the tanning process, which is as low as 10%–15% [23, 24]. As a consequence, the tanning of leather could be considered as a controllable dehydration process, especially in consideration of that chrome tanning relies on the coordination of  $\text{Cr}^{3+}$  with the carboxyls ( $-\text{COOH}$ ) of raw hide, which significantly suppresses the affinity towards water by sealing the hydrophilic groups of  $-\text{COOH}$  [5, 25, 26]. Investigations carried out by Hernandez-Serrano et al. also supported our hypothesis, which utilized terahertz time-domain spectroscopy to systematically demonstrate the importance of water content in determining leather quality [27]. On the other hand, the porosity of tanned leather was often found to significantly increase as compared with that of the raw hide [28, 29], which is actually the consequence of dehydration of raw hide. Therefore, if the necessity of raw hide converted to leather is not the formation of cross-linkage among collagen fibers but the regulation of water content in raw hide, the essence of leather making can be regarded as a controllable dehydration process of raw hide, which is accompanied with increased dispersity of collagen fibers in raw hide. Based on this different viewpoint of leather making, polar organic solvent is more preferred alternative than chrome tanning to achieve more efficient controllable dehydration of raw hide [30,

31]. However, breaking the water concentration equilibrium between raw hide and polar organic solvent is a critical challenge for realizing controllable deep dehydration of raw hide using polar organic solvent. At the initial dehydration stage, the water contained in the raw hide will transport into the organic solvent under the driving force of water concentration difference between the raw hide and organic solvent. Along with the proceeding of dehydration, the water concentration between the raw hide and solvent will gradually reach the equilibrium, which prevents the further transportation of water molecules from raw hide into organic solvent. To enable further dehydration of raw hide, the used solvent containing dehydrated water has to be replaced by the fresh solvent in order to re-establish sufficient water concentration difference between raw hide and solvent [32]. By doing so, a deep dehydration of raw hide is permitted due to the breaking of water concentration equilibrium established between raw hide and solvent. However, this multiple-steps progressive dehydration approach inevitably generated a huge amount of organic effluents containing both water and ethanol. Due to the presence of water, the resulting organic effluents cannot be directly reused before their regeneration, while the separation of pure organic solvent from these organic effluents is an unfortunately intensive-energy consumption process [33–36]. Therefore, leather making based on dehydration using organic solvent is far from an eco-friendly and sustainable manufacture process, although the dehydration approach eliminates discharge of chromium effluent. At present, it is highly desired while extremely challenging to develop a brand-new, recyclable, and high-performance dehydration systems for achieving environmental benign chrome-free leather.

Herein, we designed self-driven directional dehydration (SDD) composite media to enable controllable deep dehydration of raw hide, and successfully realized eco-friendly chrome-free leather making with non-cross-linkage required. The designed SDD composite media was comprised of anhydrous ethanol and molecular sieve (3A activated zeolite powder with the pore size of 3 Å). For the SDD composite media, the solvent component of ethanol played the role of dehydration to drive the water molecules to migrate out of raw hide, and the solid component of 3A activated zeolite powder worked as size-sieving reservoirs that permitted selective entrance and storage of water molecules with smaller kinetic diameter (2.6 Å), while strictly repelling ethanol molecules with larger kinetic diameter (4.4 Å) [33, 37, 38]. The role of 3A activated zeolite powder as size-sieving reservoirs was able to efficiently break the water concentration equilibrium between raw hide and ethanol contained in the SDD composite media, and therefore successfully

established a constant declined water concentration gradient from raw hide to ethanol, which constantly drove water molecules to transfer out of raw hide, thus allowing for continuous directional dehydration from raw hide to ethanol and further into the 3A activated zeolite powder. After the dehydration with the SDD composite media, a surface hydrophobic treatment was carried out to endow the dehydrated hide with water-repellency and durable leather-like properties. Based on the rational design of SDD composite media, we realized environmentally benign manufacture of chrome-free leather by the self-driven directional dehydration of raw hide. The as-prepared eco-friendly chrome-free leather was free from the utilization of tanning agent, which provided evident superiority in thermal stability by exhibiting considerably lower shrinkage ratio than that of chrome-tanned leather. For the used SDD composite media, the solid component of 3A activated zeolite powder and the solvent component of ethanol were easily separated by a simple filtration. The used 3A activated zeolite powder was facilely activated by thermal removal of stored water, and combined with the recovered ethanol as composite media for reuse of dehydration. The facilely recyclable SDD composite media ensured an environmentally benign leather manufacture process with a complete elimination of any discharged effluent that contains tanning agent or other chemicals. In summary, this report provided a brand-new strategy for eco-friendly chrome-free leather manufacture, which not only avoided the use of chromium to cause concerned environmental issue but also provided a feasible approach in practice for realizing sustainable manufacture process of leather industry.

## 2 Experimental

### 2.1 Materials

The raw hides and chrome-tanned leathers prepared from cattle hides were provided by National Engineering Laboratory for Clean Technology of Leather Manufacture. 3A activated zeolite powder (with the pore size of 3 Å) was purchased from Guangdong Xintao Technology Co., Ltd. (Zhuhai, China). Anhydrous ethanol was purchased from Chengdu Jinshan Chemical Reagent Co., Ltd (Chengdu, China). Silicon nanoparticle (SiO<sub>2</sub> NPs) was purchased from Aladdin Industrial Corporation (Shanghai, China). N-heptane was purchased from Chengdu Kelong Chemical Reagent Co., Ltd (Chengdu, China). Polydimethylsiloxane (PDMS) prepolymer (Sylgard 184A) and curing agent (Sylgard 184B) were purchased from Dow Corning Corporation (Midland, USA). PDMS solution (10 wt%) was prepared by dissolving 5.0 g of Sylgard 184A in 45 g of n-heptane and 0.50 g of Sylgard 184B in 4.5 g of n-heptane, respectively, followed by mixing of the two solutions. Commercial chrome tanning

agent (chrome powder) was purchased from Minfeng Chemical Reagent Co., Ltd. (Chongqing, China). Sodium chloride was purchased from Chengdu Jinshan Chemical Reagent Co., Ltd (Chengdu, China). Sodium formate was purchased from Chengdu Kelong Chemical Reagent Co., Ltd (Chengdu, China). Sodium bicarbonate was purchased from Chengdu Kelong Chemical Reagent Co., Ltd (Chengdu, China).

## 2.2 Preparation of eco-friendly chrome-free leather

### 2.2.1 Dehydration of raw hide using SDD composite media

Raw hide (300 g) and SDD composite media (consisting of 1800 g of anhydrous ethanol and 900 g of 3A activated zeolite powder) were added into a drum reactor to rotate at 20 r min<sup>-1</sup> for 210 min. The collected hide was dried at 50 °C for obtaining the SDD composite media-dehydrated hide.

After the dehydration process, the used SDD composite media was filtered to separate 3A activated zeolite powder and ethanol. After the separation of 3A activated zeolite powder from ethanol, 3A activated zeolite powder was activated at 300 °C for 3.0 h to remove the stored water dehydrated from raw hide. The activated 3A activated zeolite powder was further mixed with the recovered ethanol without any further purification to form SDD composite media, followed by reusing in the next dehydration process of raw hide.

### 2.2.2 Superhydrophobic treatment of dehydrated hide

0.24 g of SiO<sub>2</sub> NPs was added into 30 g of ethanol. Then, the SDD composite media-dehydrated hide obtained in the section of 2.2.1 was treated by vacuum filtration with the SiO<sub>2</sub> NPs suspension, followed by drying at 50 °C. Subsequently, the dehydrated hide was immersed in PDMS (10 wt%) solution for 30 min, followed by drying at 50 °C. The obtained product was eco-friendly chrome-free leather.

### 2.3 Dehydration of raw hide using anhydrous ethanol

Raw hide (300 g) and anhydrous ethanol (1800 g) were added into a drum reactor and rotated at 20 r min<sup>-1</sup> for 210 min. Then, the collected hide was dried at 50 °C for obtaining the ethanol-dehydrated hide.

### 2.4 Preparation of chrome-tanned leather

Chrome-tanned leather was prepared to compare the mechanical properties with the eco-friendly chrome-free leather. Specifically, raw hide (300 g), water (600 g), sodium chloride (42 g) and commercial chrome tanning agent (48 g) were added into a drum reactor and rotated at 20 r min<sup>-1</sup> for 240 min. Then, the pH of tanning liquor was adjusted to 3.8–4.0, followed by reacting at 40 °C with the drum reactor rotating at 20 r min<sup>-1</sup> for 20 min.

Subsequently, water at 40 °C (1200 g) was added into the drum reactor with the rotation at 20 r min<sup>-1</sup> for 120 min, followed by standing still for 10 h. After that, the drum reactor was rotated at 20 r min<sup>-1</sup> for 30 min, and then, the collected chrome-tanned leather was horsed up for 24 h, followed by toggling at 50 °C.

### 2.5 Selective adsorption of 3A activated zeolite powder to water from the water–ethanol mixture

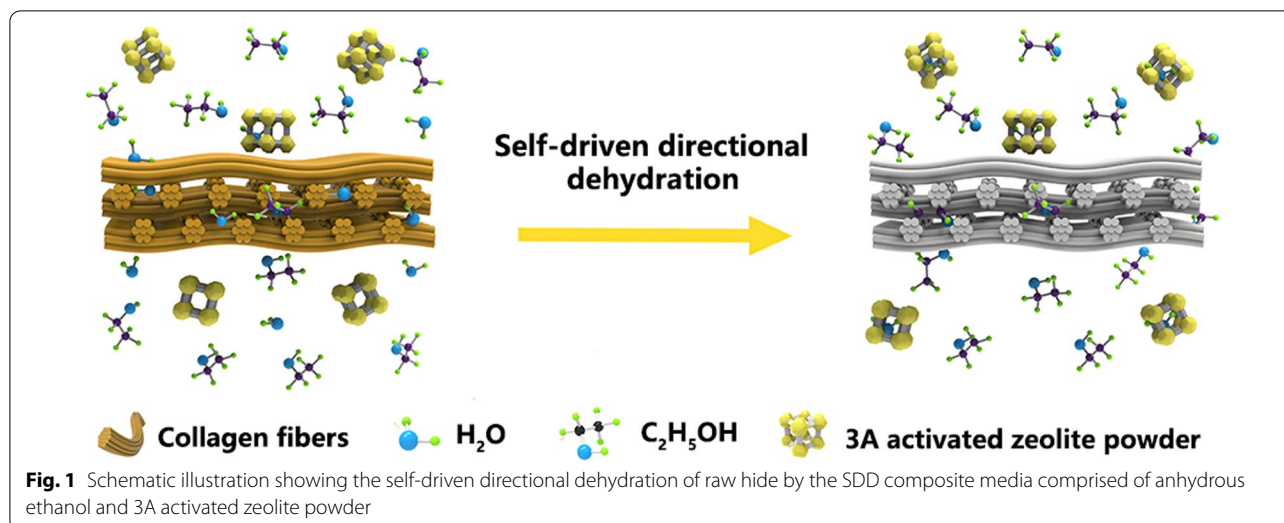
A determined amount of 3A activated zeolite powder (10, 20, 30 or 40 g) was added into 50 g of water-ethanol mixture with the water content of 5.0%, 7.5% and 10%, respectively. Subsequently, the resultant mixture was stirring at 500 rpm for 180 min, followed by filtration. The water content in the collected filtrate was measured by Karl Fischer titrator.

### 2.6 Characterization

Field-emission scanning electron microscopy (FESEM) images were taken on a scanning electron microscope (Nova Nanosem 450, FEI, USA) under 3.0 kV. X-ray diffraction (XRD) patterns of samples were recorded using an X-ray diffractometer (D8 QUEST, Bruker, Germany). Pore structures of all hides were measured by mercury intrusion porosimetry (Autopore IV 9500, Micromeritics, USA). Water content of all samples were taken on Karl Fischer titration (S-300, Heye, China). Water contact angle measurements were carried out by a contact angle goniometer (DSA30, Krüss, Germany). Tear force, tensile strength and elongation at break of all samples were tested by a mechanical properties measure instrument (AI-7000SN, Gotech, China). Thermal stability of all samples was analyzed by comparing the change of area before and after heating at 150 °C for 30 min. Water vapor permeability measurements were carried out by using a fabric water vapor permeability tester (YG(B)216 T, Yakai, China).

## 3 Results and discussion

Self-driven directional dehydration of raw hide is the critical procedure for manufacturing eco-friendly chrome-free leather. Figure 1 is the illustration showing the mechanism of self-driven directional dehydration enabled by our designed composite dehydration media (the SDD composite media). The SDD composite media consists of anhydrous ethanol and 3A activated zeolite powder with specific mass ratio (e.g., 2:1). When the raw hide is soaked in the SDD composite media, the raw hide is dehydrated by the ethanol comprised in the SDD composite media, which drives the water molecules contained in the raw hide to transfer into ethanol. For the water molecules dehydrated into ethanol, their small

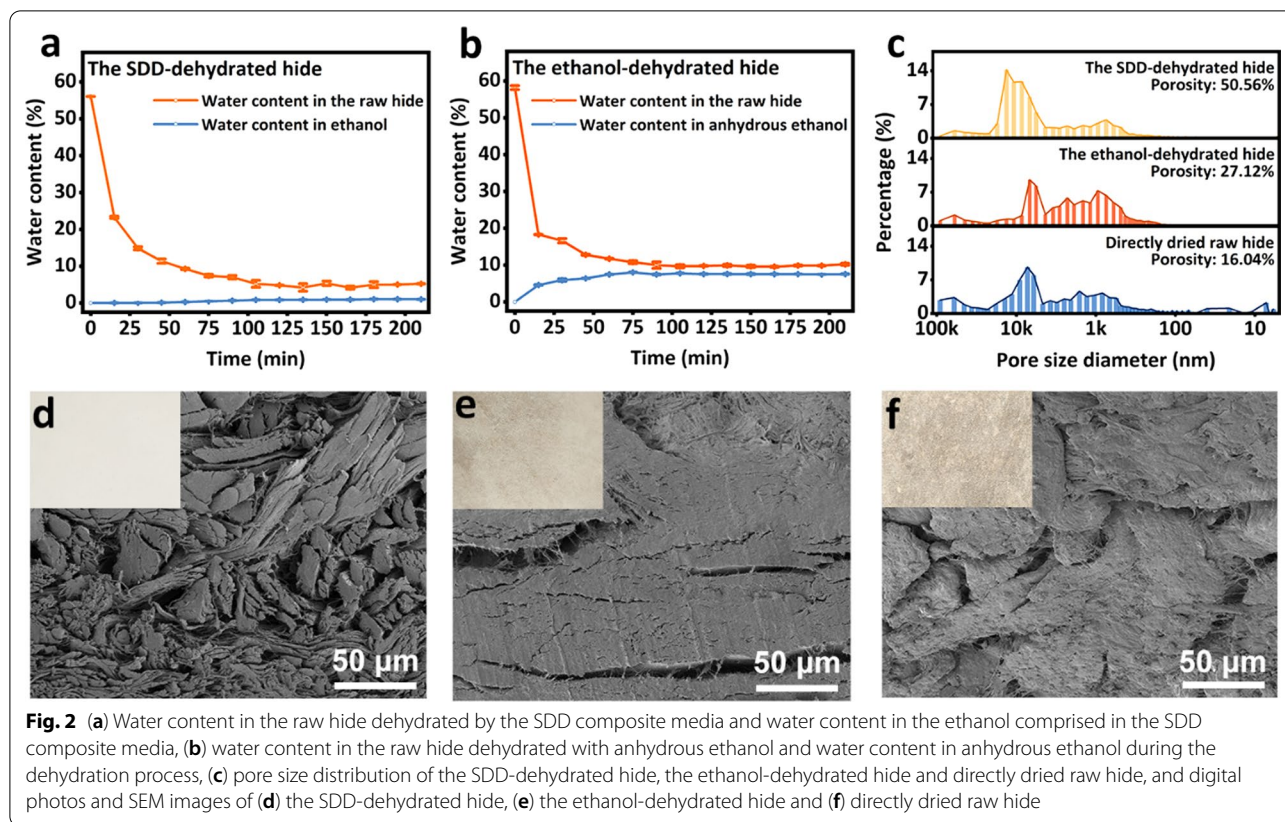


kinetic diameter (2.6 Å) allows themselves to selectively enter the porous channels (3 Å) of 3A activated zeolite powder. During this process, ethanol molecules are strictly repelled by 3A activated zeolite powder because of their kinetic diameter (4.4 Å) larger than the pore size (3 Å) of 3A activated zeolite powder. As a consequence, the 3A activated zeolite powder plays the essential role as reservoir to selectively capture the water dehydrated into ethanol, which decreases the water concentration in ethanol and therefore creates the concentration difference of water ( $\Delta C_w$ ) between raw hide and the solvent component of ethanol comprised in the SDD composite media, allowing for directional dehydration of water from raw hide to ethanol and further to the 3A activated zeolite powder. Notably, the directional dehydration is a self-driven process motivated by the  $\Delta C_w$  between raw hide-ethanol and ethanol-3A activated zeolite powder, and the self-driven directional dehydration process is able to be precisely manipulated by tuning the mass ratio of ethanol to 3A activated zeolite powder in the SDD composite media.

The SDD composite media with the mass ratio of ethanol to 3A activated zeolite powder at 2:1 was employed for the directional dehydration of raw hide. The dehydration process was simply carried out by adding raw hide and the SDD composite media into a drum reactor, followed by rotating at 20 r min<sup>-1</sup> for 210 min. As shown in Fig. 2a, the initial water content of raw hide is 56.07%, which is decreased to 5.20% after 210 min of dehydration by the SDD composite media. Although the water content of raw hide is decreased substantially, the water content in the ethanol comprised of the SDD composite media shows no obvious increase, with the initial water content of 0.30% and final water content of 1.01% at the

dehydration process of 0 min and 210 min, respectively. Evidently, the major content of water dehydrated from raw hide is selectively stored in 3A activated zeolite powder, which therefore demonstrates the directional dehydration of water from raw hide to ethanol and further to the 3A activated zeolite powder. Figure 2d shows the digital photo of the SDD composite media-dehydrated hide (SDD-dehydrated hide). The SDD-dehydrated hide shows the color of pure white, which is distinctive from the directly dried raw hide that has the color of brown. SEM observation reveals that the collage fibers in the SDD-dehydrated hide show significantly enhanced dispersity compared with the directly dried raw hide that shows serious sticking of collagen fibers. As shown in Fig. 2d, the collagen fibers contained in the SDD-dehydrated hide show typical fiber bundle appearance, and have tens of micrometers in diameter. For the directly dried raw hide, fiber bundle structure is rarely observed, and all the collagen fibers are adhered tightly showing poor distribution (Fig. 2f).

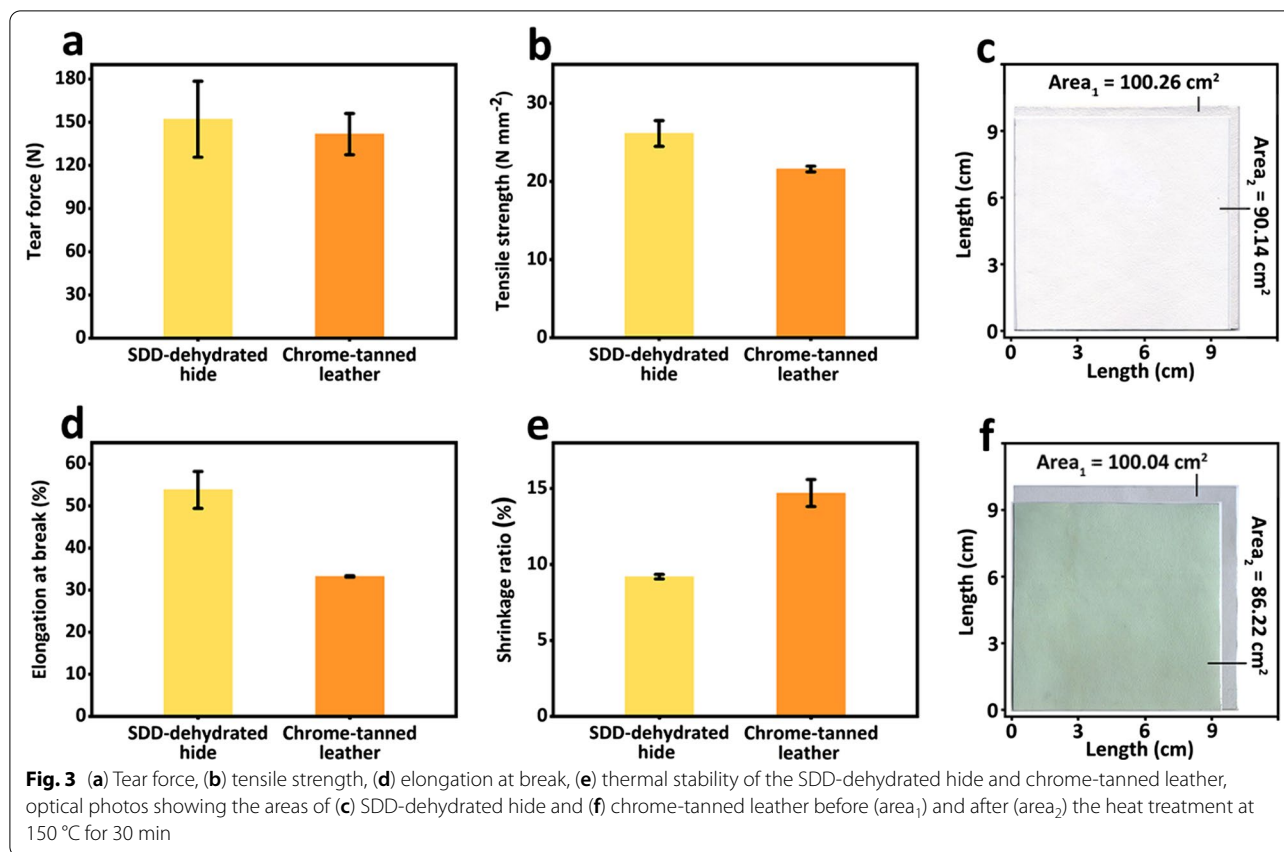
For comparison, raw hide was also dehydrated by anhydrous ethanol, and the dosage of anhydrous ethanol was control to the same with that of anhydrous ethanol contained in the SDD composite media. Figure 2b shows the water content change of raw hide during the dehydration with anhydrous ethanol. Although the water content in the raw hide is declined along with the dehydration by anhydrous ethanol, the water content in the ethanol-dehydrated hide was maintained as high as 10.23% after 210 min of dehydration with anhydrous ethanol, which is almost 2-fold of the water content in the SDD-dehydrated hide (5.20%). Evidently, the dehydration capability of anhydrous ethanol is substantially weaker than the SDD composite media. This big difference in dehydration



capability between anhydrous ethanol and the SDD composite media is a strong demonstration that the presence of 3A activated zeolite powder efficiently prevents the water concentration equilibrium established between raw hide and ethanol, which therefore guarantees constant and sufficient  $\Delta C_w$  along with the dehydration to proceed, thus enabling the SDD composite media to provide a considerably higher content of dehydration as compared with the same dosage of anhydrous ethanol. As shown in Fig. 2e, the collagen fibers contained in the ethanol-dehydrated hide shows substantially poor dispersity compared with those in the SDD-dehydrated hide. Dispersed fiber bundle structure was rarely observed in the ethanol-dehydrated hide, which attributes to that the considerably higher content of water plays the role as binder to stick the collagen fibers together. Consistent with the results of SEM observations, further porosity measurements by mercury intrusion porosimetry also confirm the drastic difference of structural porosity induced by the water content in the dehydrated hides. As shown in Fig. 2c, the porosity of SDD-dehydrated hide is as high as 50.56% while that of ethanol-dehydrated hide is merely 27.12%. Evidently, compared with anhydrous ethanol, the SDD composite media enables the raw hide to experience a considerably higher content of dehydration,

which allows for the obtaining of highly dispersed collagen fibers. As for the directly dried raw hide, the porosity is as low as 16.04%. This low porosity combined with the serious sticking of collagen fibers indicate that without a dehydration treatment, the direct drying of raw hide still fails to disperse the collagen fibers in raw hide. Above results manifest that a deep dehydration using SDD composite media is feasible to obtain well dispersed collagen fibers of raw hide.

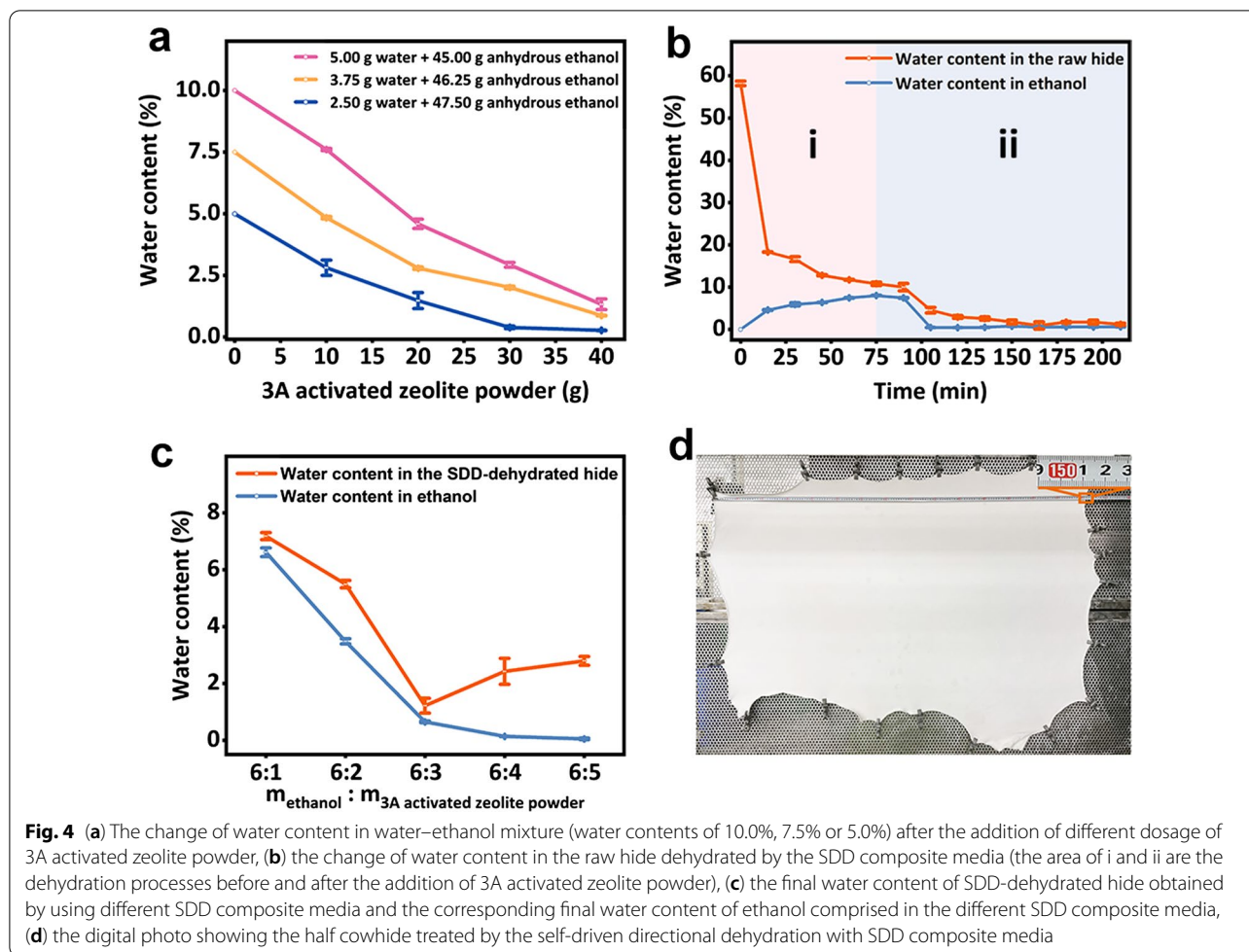
Compared with the conventional chrome-tanned leather, the SDD-dehydrated hide exhibits superiority in mechanical properties of tear force and tensile strength, which are 170.20 N and 30.15 N mm<sup>-2</sup>, respectively, accounting for 20.02% and 39.59% of enhancement when compared with the corresponding tear force (141.81 N) and tensile strength (21.60 N mm<sup>-2</sup>) of chrome-tanned leather, as shown in Fig. 3a, b. Notably, the SDD-dehydrated hide provides considerably improved thermal stability than the conventional chrome-tanned leather. Figure 3c, f show the area of SDD-dehydrated hide and chrome-tanned leather shrink after heat treatment at 150 °C for 30 min (EN ISO 17227:2002). The shrinkage ratio of SDD-dehydrated hide was as low as 9.20%, while that of chrome-tanned leather was high up to 14.70% (Fig. 3e). Thermal stability is an important critical index



for estimating the durability of leather in practical utilization. The obviously enhanced thermal stability of SDD-dehydrated hide indicates that the deep dehydration using SDD composite media is capable of providing comparable and even better leather-like properties than the conventional chrome-tanned leather. Notably, the SDD-dehydrated hide has the elongation at break of 53.8%, which meets the criteria (45%–75%) of shoe leather (ISO 20942-2019), as shown in Fig. 3d. However, the elongation at break of chrome-tanned leather was merely 33.25%, which often requires a series of post-treatment (e.g., re-tanning and fatliquoring) to improve the property of elongation at break. Evidently, without the formation of cross-linkage by chrome salt, dehydration using SDD composite media is still able to provide the raw hide with desired leather-like properties, which strongly supports our hypothesis that the leather making process can be considered as a controllable dehydration process of raw hide, accompanied with the dispersity of collagen fibers.

To unfold the self-driven directional dehydration mechanism of SDD composite media, selective adsorption experiments of 3A activated zeolite powder to water from the water-ethanol mixture were carried out.

A determined amount of 3A activated zeolite powder (10, 20, 30 or 40 g) was added into water-ethanol mixture (50 g) with the water content of 5.0%, respectively. After stirring at 180 min for 500 rpm, the water content in the corresponding filtrates was measured to be 2.81%, 1.48%, 0.79% or 0.27%, respectively, as shown in Fig. 4a. Clearly, the amount of water selectively captured from the water-ethanol mixture is increased along with the increase of 3A activated zeolite powder dosage in the SDD composite media. Enhanced water capture capability to water-ethanol mixture with higher water content (7.5% and 10%) was also observed on those SDD composite media with higher dosage of 3A activated zeolite powder. These results indicate that in the water-ethanol mixture, the selective capture capability of SDD composite media to water is facily enhanced by simply increasing the dosage of 3A activated zeolite powder comprised in the SDD composite media. We further carried out a 2-step dehydration process of raw hide through a successive addition of anhydrous ethanol and 3A activated zeolite powder in the drum reactor. As shown in Fig. 4b, the water content in the raw hide is decreased sharply from 58.20% to 18.32% after dehydration with anhydrous ethanol for 15 min, which then experiences a gradual

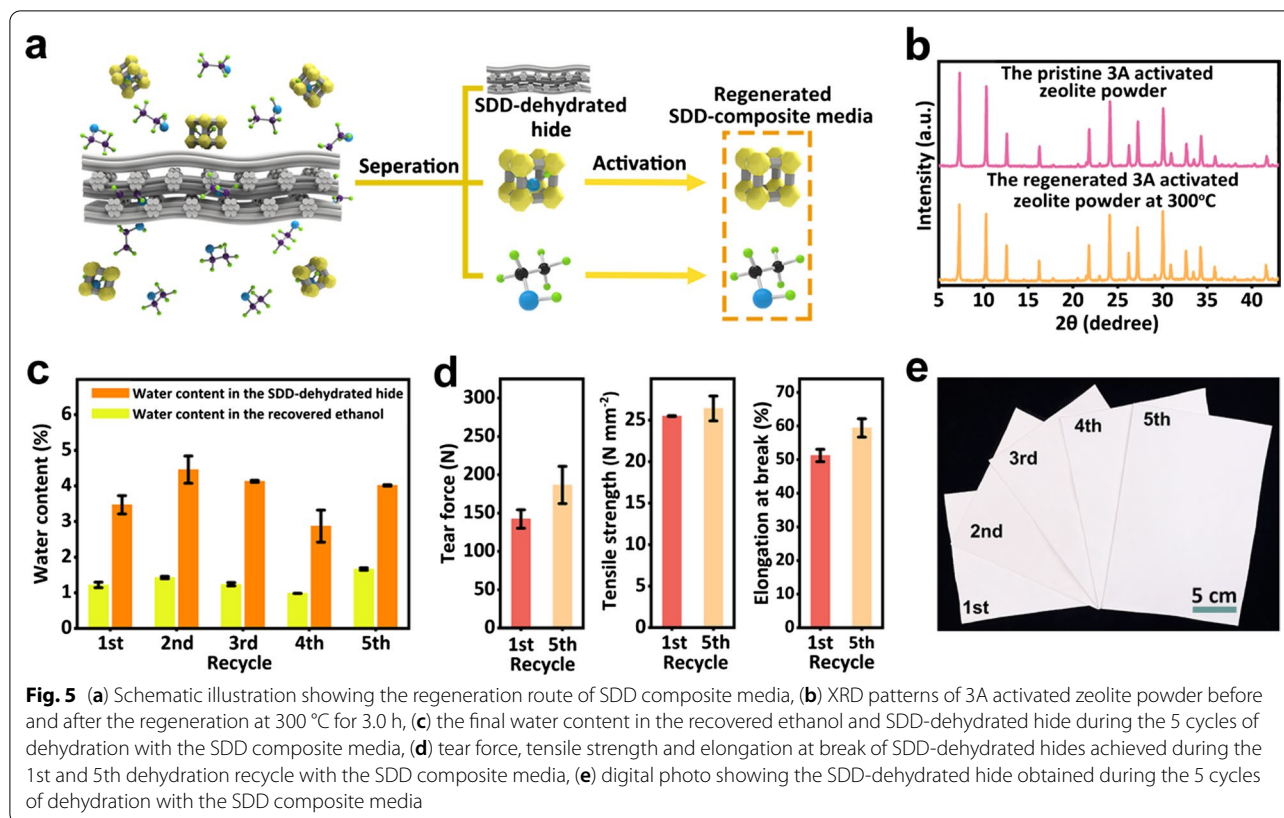


and slow decrease process in the subsequent dehydration to 75 min because of the substantially decreased  $\Delta C_w$  between raw hide and anhydrous ethanol. During the above 75 min of dehydration process, the water content in ethanol is gradually increased to 8.03% since all the water molecules dehydrated from raw hide enter into ethanol. Notably, the water content in the raw hide shows a more evident decrease after the addition of 3A activated zeolite powder into the ethanol. Upon the addition of 3A activated zeolite powder into the ethanol at 75 min, the water content in ethanol begins to decrease rather than increase, and quickly decreases to 0.48% at 105 min, keeping the low water content (0.65%) until to the end of the dehydration process (210 min). These results therefore manifest that the addition of 3A activated zeolite powder indeed break the  $\Delta C_w$  established between raw hide and ethanol via selective capture of dehydrated water in ethanol, which promotes the further dehydration of raw hide. Actually, we carried out a series of above 2-step dehydration process of raw hide by added varied amount of 3A activated zeolite powder into the

pre-added ethanol. As shown in Fig. 4c, the final water content in the dehydrated hide and ethanol is rationally controlled. These results confirm the feasibility and convenience of using the SDD composite media with varied mass ratio of ethanol to 3A activated zeolite powder for accomplishing controllable self-driven directional dehydration. Figure 4d shows the digital photo of half cowhide treated by the self-driven directional dehydration with SDD composite media, which suggests the great potential of this new conceptual dehydration strategy for practical application. Above results suggest that regulating the water content in raw hide is feasible to accomplish leather making without cross-linkage formation or any tanning agent involved.

Importantly, the used SDD composite media was able to be facily regenerated and recycled for the dehydration of raw hide. As illustrated in Fig. 5a, the used SDD composite media was filtered to separate 3A activated zeolite powder and recover ethanol. The collected 3A activated zeolite powder was further activated and further mixed with the recovered ethanol to form the SDD

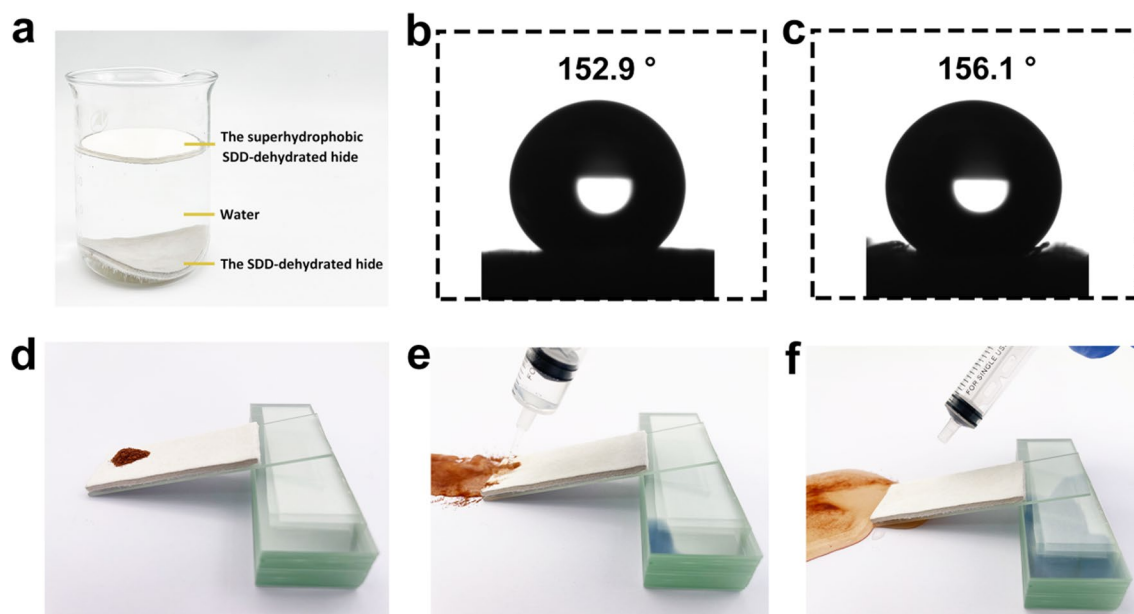




composite media for reuse. Based on the Karl Fischer titration, the water content in the recovered ethanol was as low as 1.01%, indicating that the water dehydrated from raw hide is indeed selectively adsorbed into the 3A activated zeolite powder. The collected 3A activated zeolite powder was further activated at 300 °C for 3.0 h to remove the stored water molecules inside the channels of 3A activated zeolite powder. Based on the XRD analysis (Fig. 5b), the characteristic peaks of 3A activated zeolite powder at  $2\theta$  of 7.35°, 10.32°, 24.14°, 27.27° and 30.09° show no obvious change, indicating the crystal structure of 3A activated zeolite powder is intact during the activation at 300 °C. The regenerated SDD composite media was successfully reused for the self-driven directional dehydration of raw hide. As shown in Fig. 5c, the water content in raw hide was still reduced to 3.47% after the dehydration with the regenerated SDD composite media for 150 min. In addition, a 2-step dehydration process of raw hide was also carried out by using the activated 3A activated zeolite powder and the recovered ethanol. As shown in Additional file 1: Fig. S1, the declined water content in raw hide and increased water content in the recovered ethanol were observed before the addition of activated 3A activated zeolite powder. After the addition of activated 3A activated zeolite powder at 75 min,

an evident decrease of water content was observed both in raw hide and the recovered ethanol. The changes of water content in raw hide and the recovered ethanol are consistent with those observed during the dehydration of raw hide using the fresh SDD composite media, which manifests that the SDD composite media recovers the self-driven directional dehydration capability after the regeneration treatment. Actually, we evaluated the reusability of SDD composite media for 5 cycles. As shown in Fig. 5c, a deep dehydration of raw hide was guaranteed during the cycles. In the 5th cycle, the water content in the SDD-dehydrated hide was as low as 4.02%, and the obtained dehydrated hide still presents outstanding physical properties comparable to those of dehydrated hide obtained in the 1st cycle, with the tear force of 186.66 N, the tensile strength of 26.40 N mm<sup>-2</sup> and the elongation at break of 59.45% (Fig. 5d). Figure 5e shows the SDD-dehydrated hides obtained from each cycle of dehydration with the SDD composite media.

The SDD-dehydrated hide will re-adsorb water to lose the leather-like properties upon exposed to the moisture environment. Therefore, a surface hydrophobic treatment was applied on the SDD-dehydrated hide for obtaining water-repellency so as to maintain long-lived leather-like properties. Specifically, SiO<sub>2</sub>



**Fig. 6** (a) Digital photo showing the SDD-dehydrated hide sinking in water and the superhydrophobic SDD-dehydrated hide floating on water, digital photos showing the water contact angle of (b) grain surface and (c) flesh surface of the superhydrophobic SDD-dehydrated hide, (d–f) digital photos showing the self-cleaning ability of the superhydrophobic SDD-dehydrated hide

NPs was utilized to enhance the surface roughness of SDD-dehydrated hide, followed by coating PDMS to reduce the surface energy. As shown in Fig. 6a, the as-treated SDD-dehydrated hide is able to float on the water, and shows the water contact angle of  $152.9^\circ$  (Fig. 6b) and  $156.1^\circ$  (Fig. 6c) at the grain surface and flesh surface, respectively, indicating its superhydrophobicity. As shown in Fig. 6d–f, the superhydrophobic SDD-dehydrated hide provides convenience for surface cleaning due to its self-cleaning ability. The water vapor permeability of the SDD-dehydrated hide and superhydrophobic SDD-dehydrated hide were measured to be  $48.09 \text{ g m}^{-2} \text{ h}^{-1}$  and  $45.50 \text{ g m}^{-2} \text{ h}^{-1}$ , respectively, which indicates that the surface hydrophobic treatment has limited impact on the water vapor permeability of the manufactured eco-friendly leather. Additional file 1: Table S1 summarizes the physical properties of superhydrophobic SDD-dehydrated hide, which fully meet the criteria of shoe leather (ISO 20942–2019).

As we have demonstrated above, the SDD-dehydrated hide with outstanding leather-like properties was successfully prepared without the utilization of any cross-linking agent, and the SDD composite media employed for controllable deep dehydration of raw hide was fully recovered and recyclable. Therefore, the eco-friendly leather manufacture process as well

as leather product are feasible to achieve by using the new conceptual self-driven directional dehydration strategy provided by the present investigation.

#### 4 Conclusions

In summary, we have developed a brand-new leather manufacture approach to promote the sustainable development of leather industry, which is based on the establishment of self-driven directional dehydration (SDD) composite media and its utilization for controllable deep dehydration of raw hide. The established SDD composite media was comprised of 3A activated zeolite powder and anhydrous ethanol, which was able to create stable water concentration gradient between raw hide and ethanol, thus allowing for the continuous self-driven directional dehydration of raw hide. The SDD-dehydrated hide exhibited well dispersed collagen fibers, increased porosity and thermal stability. After a superhydrophobic treatment, the resultant superhydrophobic SDD-dehydrated hide exhibited outstanding water repellency and durable leather-like properties. Notably, the SDD composite media was conveniently recycled for the dehydration of raw hide. Therefore, our investigations provided a promising way for realizing environmentally benign leather manufacture with a complete elimination of tanning agent-containing effluent as well as facily obtaining eco-friendly chrome-free leather with high quality.

## Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s42825-022-00089-0>.

**Additional file 1: Fig. S1.** The change of water content in the raw hide dehydrated by the regenerated SDD composite media and the water content in the recovered ethanol comprised in the regenerated SDD composite media (the area of i and ii are the dehydration processes before and after the addition of the 3A activated zeolite powder). **Table S1.** Tear force, tensile strength, elongation at break and shrinkage ratio of the super-hydrophobic SDD-dehydrated hide.

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### Author contributions

XH and BS conceived the idea. YH, NX and HP carried out materials preparation. YH and BH carried out materials characterization. YH and HX carried out the manufacture of eco-friendly chrome-free leather. YH, XH and BS drafted the manuscript. All authors analyzed the experimental results. All authors read and approved the final manuscript.

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### Availability of data and materials

All data from this study are presented in the paper and the supplementary material.

### Declarations

### Competing interests

The authors declare that they have no competing interests.

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### References

- Kim DH, Kim YS, Wu J, Liu ZJ, Song JZ, Kim HS, Huang YGY, Hwang KC, Rogers JA. Ultrathin silicon circuits with strain-isolation layers and mesh layouts for high-performance electronics on fabric, vinyl, leather, and paper. *Adv Mater.* 2009;21:3703. <https://doi.org/10.1002/adma.20090405>.
- Jiang ZC, Ding W, Xu SG, Remon J, Shi B, Hu CW, Clark JH. A 'Trojan horse strategy' for the development of a renewable leather tanning agent produced via an  $AlCl_3$ -catalyzed cellulose depolymerization. *Green Chem.* 2020;22:316–21. <https://doi.org/10.1039/c9gc03538a>.
- Rosu L, Varganici CD, Crudu AM, Rosu D, Bele A. Ecofriendly wet-white leather vs. conventional tanned wet-blue leather. A photochemical approach. *J Clean Prod.* 2018;177:708–20. <https://doi.org/10.1016/j.jclepro.2017.12.237>.
- Li HF, Zheng W, Xiao HZ, Hao BC, Wang YJ, Huang X, Shi B. Collagen fiber membrane-derived chemically and mechanically durable superhydrophobic membrane for high-performance emulsion separation. *J Leather Sci Eng.* 2021;3:20. <https://doi.org/10.1186/s42825-021-00060-5>.
- Krishnamoorthy G, Sadulla S, Sehgal PK, Mandal AB. Green chemistry approaches to leather tanning process for making chrome-free leather by unnatural amino acids. *J Hazard Mater.* 2012;215:173–82. <https://doi.org/10.1016/j.jhazmat.2012.02.046>.
- Wu B, Mu CD, Zhang GZ, Lin W. Effects of  $Cr^{3+}$  on the structure of collagen fiber. *Langmuir.* 2009;25:11905–10. <https://doi.org/10.1021/la901577j>.
- Liu M, Ma JZ, Lyu B, Gao DG, Zhang J. Enhancement of chromium uptake in tanning process of goat garment leather using nanocomposite. *J Clean Prod.* 2016;133:487–94. <https://doi.org/10.1016/j.jclepro.2016.04.156>.
- Wang XC, Sun SW, Zhu X, Guo PY, Liu XH, Liu CL, Lei M. Application of amphoteric polymers in the process of leather post-tanning. *J Leather Sci Eng.* 2021;3:9. <https://doi.org/10.1186/s42825-021-00050-7>.
- Covington AD. Modern tanning chemistry. *Chem Soc Rev.* 1997;26:111–26. <https://doi.org/10.1039/cs9972600111>.
- Orukko RO, Selvarajan R, Ogola HJO, Edokpayi JN, Odiyo JO. Contemporary and future direction of chromium tanning and management in sub Saharan Africa tanneries. *Process Saf Environ Protect.* 2020;133:369–86. <https://doi.org/10.1016/j.psep.2019.11.013>.
- China CR, Maguta MM, Nyandoro SS, Hilonga A, Kanth SV, Njau KN. Alternative tanning technologies and their suitability in curbing environmental pollution from the leather industry: A comprehensive review. *Chemosphere.* 2020;254:126804. <https://doi.org/10.1016/j.chemosphere.2020.126804>.
- Gao DG, Wang PP, Shi JB, Li F, Li WB, Lyu B, Ma JZ. A green chemistry approach to leather tanning process: cage-like octa (aminosilsesquioxane) combined with tetrakis (hydroxymethyl) phosphonium sulfate. *J Clean Prod.* 2019;229:1102–11. <https://doi.org/10.1016/j.jclepro.2019.05.008>.
- Cao S, Liu B, Cheng BZ, Lu FP, Wang YP, Li Y. Mechanisms of Zn (II) binded to collagen and its effect on the capacity of eco-friendly Zn-Cr combination tanning system. *J Hazard Mater.* 2017;321:203–9. <https://doi.org/10.1016/j.jhazmat.2016.09.016>.
- Krishnamoorthy G, Sadulla S, Sehgal PK, Mandal AB. Greener approach to leather tanning process: D-Lysine aldehyde as novel tanning agent for chrome-free tanning. *J Clean Prod.* 2013;42:277–86. <https://doi.org/10.1016/j.jclepro.2012.11.004>.
- Yu Y, Wang YN, Ding W, Zhou JF, Shi B. Preparation of highly-oxidized starch using hydrogen peroxide and its application as a novel ligand for zirconium tanning of leather. *Carbohydr Polym.* 2017;174:823–9. <https://doi.org/10.1016/j.carbpol.2017.06.114>.
- Gao DG, Cheng YM, Wang PP, Li F, Wu YK, Lyu B, Ma JZ, Qin JB. An eco-friendly approach for leather manufacture based on P(POSS-MAA)-aluminum tanning agent combination tanning. *J Clean Prod.* 2020;257:120546. <https://doi.org/10.1016/j.jclepro.2020.120546>.
- Hao DY, Wang XCA, Liu XH, Su RR, Duan ZJ, Dang XG. Chrome-free tanning agent based on epoxy-modified dialdehyde starch towards sustainable leather making. *Green Chem.* 2021;23:9693–703. <https://doi.org/10.1039/d1gc03472c>.
- Ding W, Yi YD, Wang YN, Zhou JF, Shi B. Peroxide-periodate co-modification of carboxymethylcellulose to prepare polysaccharide-based tanning agent with high solid content. *Carbohydr Polym.* 2019;224:115169. <https://doi.org/10.1016/j.carbpol.2019.115169>.
- Jia XJ, Zhang CX, Chattha SA, Peng BY. A salt-free pickling chrome tanning technology: pretreatment with the collective polyoxyethylene diepoxy ether and urotropine. *J Clean Prod.* 2020;244:118706. <https://doi.org/10.1016/j.jclepro.2019.118706>.
- Zhang ZT, Liu Y, Wang JC, Xie TL, Sun LY, Li ZJ. A chrome-free combination tanning strategy: based on silicic acid and plant tannin. *J Leather Sci Eng.* 2021;3:15. <https://doi.org/10.1186/s42825-021-00058-z>.

21. Lofrano G, Meric S, Zengin GE, Orhon D. Chemical and biological treatment technologies for leather tannery chemicals and wastewaters: a review. *Sci Total Environ.* 2013;461:265–81. <https://doi.org/10.1016/j.scitotenv.2013.05.004>.
22. Cassano A, Molinari R, Romano M, Deioli E. Treatment of aqueous effluents of the leather industry by membrane processes-a review. *J Membr Sci.* 2001;181:111–26. [https://doi.org/10.1016/S0376-7388\(00\)00399-9](https://doi.org/10.1016/S0376-7388(00)00399-9).
23. Santos LM, Gutterres M. Reusing of a hide waste for leather fatliquoring. *J Clean Prod.* 2007;15:12–6. <https://doi.org/10.1016/j.jclepro.2006.01.025>.
24. Reich G. From collagen to leather-the theoretical background. Freiburg: BASF Service Center; 2007. p. 2007.
25. Jiang ZC, Xu SG, Ding W, Gao M, Fan JJ, Hu CW, Shi B, Clark JH. Advanced masking agent for leather tanning from stepwise degradation and oxidation of cellulose. *Green Chem.* 2021;23:4044–50. <https://doi.org/10.1039/d1gc01264a>.
26. Jiang YP, Li JX, Liu FM, Zhang ZC, Li ZJ, Yang MB, Liu LX. The effects of surface modification using O<sub>2</sub> low temperature plasma on chrome tanning properties of natural leather. *J Ind Text.* 2019;49:534–47. <https://doi.org/10.1177/1528083718804205>.
27. Hernandez-Serrano AI, Corzo-Garcia SC, Garcia-Sanchez E, Alfaro M, Castro-Camus E. Quality control of leather by terahertz time-domain spectroscopy. *Appl Opt.* 2014;53:7872–6. <https://doi.org/10.1364/AO.53.007872>.
28. He X, Wang YN, Zhou JF, Wang HB, Ding W, Shi B. Suitability of pore measurement methods for characterizing the hierarchical pore structure of leather. *J Am Leather Chem.* 2019;114:41–7.
29. He X, Ding W, Zeng YH, Yu Y, Zhou JF, Shi B. Insight into the correlations between fiber dispersion and physical properties of chrome tanned leather. *J Am Leather Chem.* 2020;115:23–9.
30. Henderson RK, Jimenez-Gonzalez C, Constable DJC, Alston SR, Inglis GGA, Fisher G, Sherwood J, Binks SP, Curzons AD. Expanding GSK's solvent selection guide-embedding sustainability into solvent selection starting at medicinal chemistry. *Green Chem.* 2011;13:854–62. <https://doi.org/10.1039/c0gc00918k>.
31. Bacardit A, Baquero G, Sorolla S, Olle L. Evaluation of a new sustainable continuous system for processing bovine leather. *J Clean Prod.* 2015;101:197–204. <https://doi.org/10.1016/j.jclepro.2015.04.012>.
32. He X, Huang YW, Xiao HZ, Xu XZ, Wang YJ, Huang X, Shi B. Tanning agent free leather making enabled by the dispersity of collagen fibers combined with superhydrophobic coating. *Green Chem.* 2021;23:3581–7. <https://doi.org/10.1039/d1gc00380a>.
33. Gabrus E, Witkiewicz K, Nastaj J. Modeling of regeneration stage of 3A and 4A zeolite molecular sieves in TSA process used for dewatering of aliphatic alcohols. *Chem Eng J.* 2018;337:416–27. <https://doi.org/10.1016/j.cej.2017.12.112>.
34. Agueda VI, Delgado JA, Uguina MA, Sotelo JL, Garcia A. Column dynamics of an adsorption-drying-desorption process for butanol recovery from aqueous solutions with silicalite pellets. *Sep Purif Technol.* 2013;104:307–21. <https://doi.org/10.1016/j.seppur.2012.11.036>.
35. Gadalla MA, Olujic Z, Jansens PJ, Jobson M, Smith R. Reducing CO<sub>2</sub> emissions and energy consumption of heat-integrated distillation systems. *Environ Sci Technol.* 2005;39:6860–70. <https://doi.org/10.1021/es049795q>.
36. Halvorsen IJ, Skogestad S. Energy efficient distillation. *J Nat Gas Sci Eng.* 2011;3:571–80. <https://doi.org/10.1016/j.jngse.2011.06.002>.
37. Vane AM. Separation technologies for the recovery and dehydration of alcohols from fermentation broths. *Biofuels Bioprod Biorefining.* 2008;2:553–88. <https://doi.org/10.1002/bbb.108>.
38. Al-Asheh S, Banat F, Al-Lagtah N. Separation of ethanol-water mixtures using molecular sieves and biobased adsorbents. *Chem Eng Res Des.* 2004;82:855–64. <https://doi.org/10.1205/0263876041596779>.

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