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Green Chemistry

COMMUNICATION

A novel 'Trojan Horse Strategy' for the development of a renewable leather tanning agent produced via an $AlCl_3$-catalyzed cellulose depolymerization

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The development of renewable and non-toxic tanning agents substantially contributes toward the sustainable expansion of the leather industry. Herein, we report a green methodology to synthesize a novel tanning agent consisting of Al-oligosaccharides complexes produced via an efficient $AlCl_3$-catalyzed cellulose depolymerization. Our experimental procedure allowed the production of a high purity tanning agent by the effective removal of the cellulose-decomposed small oxygenates and macromolecular oligosaccharides, via a liquid-liquid extraction using THF as the solvent. This also promoted the decolorization of the leather and enabled the efficient penetration of Al into the collagen matrix of skin. On this matter, experimental work combined with theoretical modeling were used to elucidate the tanning mechanism. In a first step, $[Al(OH)_1(H_2O)_4]^{2+}$ and $[Al(OH)_2(H_2O)_2]^{+}$ species weakly interacted or coordinated with the O-1 bond of the oligosaccharides produced. This interaction efficiently prevented the overload of Al species onto the leather surface, thus enhancing their penetration into leather matrix. Then, the active Al species were released from the Al-oligosaccharides complex and strongly coordinated with the $–NH_2$ groups of the collagen fibers present in the leather, which helped to stabilize the fiber bundles, and therefore, contributed to achieve a satisfactory tanning performance.

Leather products, considered common life necessities, are used in many applications ranging from clothing, footwear and upholstery [1, 2] to advanced materials, such as membranes and shielding materials.[3, 4] Leather is made up of animal skin, which can be regarded as one kind of biomass, thus being a sustainable resource for the renewable production of materials. Animal skin mainly consists of collagen, a fibrillar protein comprising a three-dimensional and hierarchical structure. Precisely, it is composed by glycine, glutamic acid, aspartic acid, and other amino acids.[5] However, before raw skin can be used for commercial applications, it must be subjected to a tanning process in order to enhance its physicochemical properties. This tanning process involves several crosslinking reactions between the tanning agent and the active groups ($-NH_2$ and -COOH) in the collagen matrix, aiming at improving the dispersion and fixation of the collagen fibers. This procedure not only endows the leather with a high resistance against putrefaction, chemicals and heat but also with high mechanical strength. Mineral salts, such as chromium, aluminum, titanium, iron and zirconium salts, are widely used as tanning agents due to their favorable tanning effect and availability.[6-9] At present, chrome salts (Cr(III)) are the most used tanning agent worldwide. However, their use is becoming more and more restrictive, due to their potential risk to human health and environmental issues, especially when Cr(III) is oxidized to Cr(VI), which is a human carcinogen.[10-12] Therefore, the development of an eco-friendly chrome-free metal, tanning agent is of paramount importance for the sustainable development of the leather science and industry. In addition, because of the high coordination ability of metals as the tanning agents, the metal species can strongly react with the collagen fibers in the initial stage of the tanning process, leading to a metal overload on the leather surface, which results in a non-uniform penetration and a consequently weak tanning effect.[13] This issue can be solved using a masking ligand in a two-step process, in which, firstly the metal ion, as masked complexes, is transferred to the skin matrix prior to its reaction on the leather surface, and secondly, the active metal ion is released into the collagen matrix, thus providing its tanning performance.

Cellulose, as the most abundant component in renewable lignocellulose biomass, is one of the most copious natural biopolymers on the Earth. [14] As such, the conversion of this bio-based feedstock into chemicals, materials and energy is highly recommended to achieve a sustainable production of these

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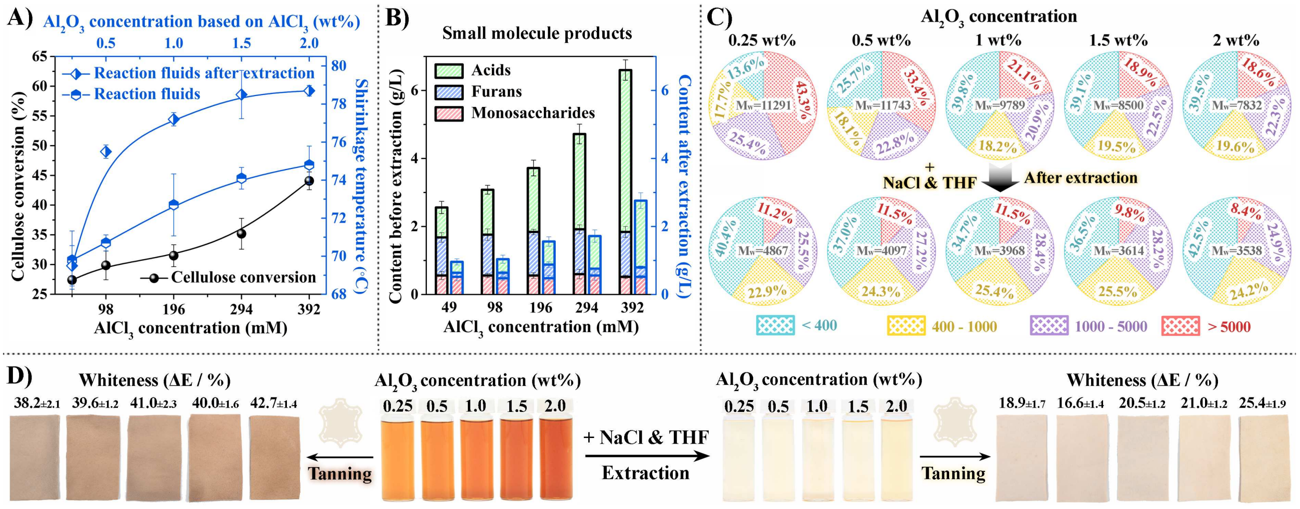

Fig. 1 A) Effect of $AlCl_3$ on the conversion of microcrystalline cellulose at 180 °C and shrinkage temperature (T_s) of leathers tanned by the corresponding hydrolysates; B) Content of the small molecular weight products and C) molecular weight distribution of the oligosaccharides produced from cellulose before and after extraction; D) Effect of the solvent extraction on the color of hydrolysates and leather tanned.

commodities. However, the high polymerization degree (2500 to 14000) of this glucose-composed bio-polymer greatly hinders its conversion for further applications.[15] A possible solution to overcome this issue is the use of catalysts. In particular, chloride salts, which are economical and less corrosive than mineral acids, have shown an excellent performance on cellulose depolymerization.[16, 17] Particularly, $AlCl_3$ was reported to be highly effective for the catalytic cleavage of the glycosidic bonds in cellulose. This is the result of both species, Al^{3+} and Cl^-, being capable of synergistically breaking the resistant hydrogen bonds in cellulose.[18, 19] In a previous work, an $AlCl_3$-H_2O system was used for the conversion of cellulose in corncob residue to carboxylic acids. [18, 19] Although cellulose was completely depolymerized using $AlCl_3$ as the catalyst, nearly half of the obtained products were soluble oligosaccharides.[20] Therefore, owing to the potential coordination ability of Al^{3+} with the abundant hydroxyl groups of the oligosaccharides produced, this reaction mixture is promising as a sustainable and renewable leather tanning agent. Given this background, the objective of this work is the development of a novel 'Trojan Horse Strategy' to employ $AlCl_3$ as not only the catalyst for cellulose degradation, but also the coordination center for tanning, making full use of the Al^{3+} ions. In this manner, the oligosaccharides produced from cellulose depolymerization can be used as a 'renewable masking ligand' to achieve a controllable release of the Al^{3+} species in order to improve their penetration into the skin matrix, avoiding their deposition onto the leather surface.

Initially, the effect of $AlCl_3$ on the hydrothermal degradation of microcrystalline cellulose (MC) was investigated at 180 °C using an Anton Paar microwave reactor. A synergistic effect was observed between $AlCl_3$ Lewis acid and the protons (H^+) produced during cellulose decomposition, which resulted in a greater cellulose conversion. [21, 22] Besides, increasing the concentration of $AlCl_3$ increased the reaction rate of the depolymerization reactions (Fig. 1A). After reaction, oligosaccharides with a relatively high average molecular weight were the predominant products in the hydrolysates, while less than one third of the converted cellulose was decomposed into small molecular weight species. The Al^{3+}-rich hydrolysates produced were tested as tanning agents without any further purification, i.e. including all the degradation products from cellulose. In these tests, pickled cattle skin was used as the raw material for the tanning process in a drum. To better describe the effect of the Al species during the tanning procedure, their concentration was calculated as Al_2O_3, based on the $AlCl_3$ dosage used in the experiments. The shrinkage temperature (T_s) of leather is an important parameter to characterize the tanning performance.[23] A 5 °C increment of the (T_s) was achieved with increasing Al_2O_3 equivalent concentration from 0.25 to 2 wt%, demonstrating the absolutely decisive role of Al species in the crosslinking reactions, in which Al reacted with diverse groups (e.g. $-NH_2$ and $-COOH$) in the collagen matrix during the tanning procedure. Besides, the absorption ratio of the carbon from the tanning agent (reaction liquid produced from cellulose degradation) substantially increased with increasing dosage of Al^{3+} (Table S1), which confirms the coordination of the Al^{3+} species with the oligosaccharides produced from cellulose.

Despite these good results, the red-brown color of this renewable tanning agent resulted in leather staining. In particular, a difference in color of around 40% was observed (ΔE, lower ΔE value means higher whiteness) (Fig. 1C), which limits the use value of the treated leather.[1] Therefore, to increase the whiteness of the tanned leather, an extraction system was developed to remove the colored components (e.g. furans) from the tanning agent. In particular, NaCl and tetrahydrofuran (THF) were added to the cellulose-derived

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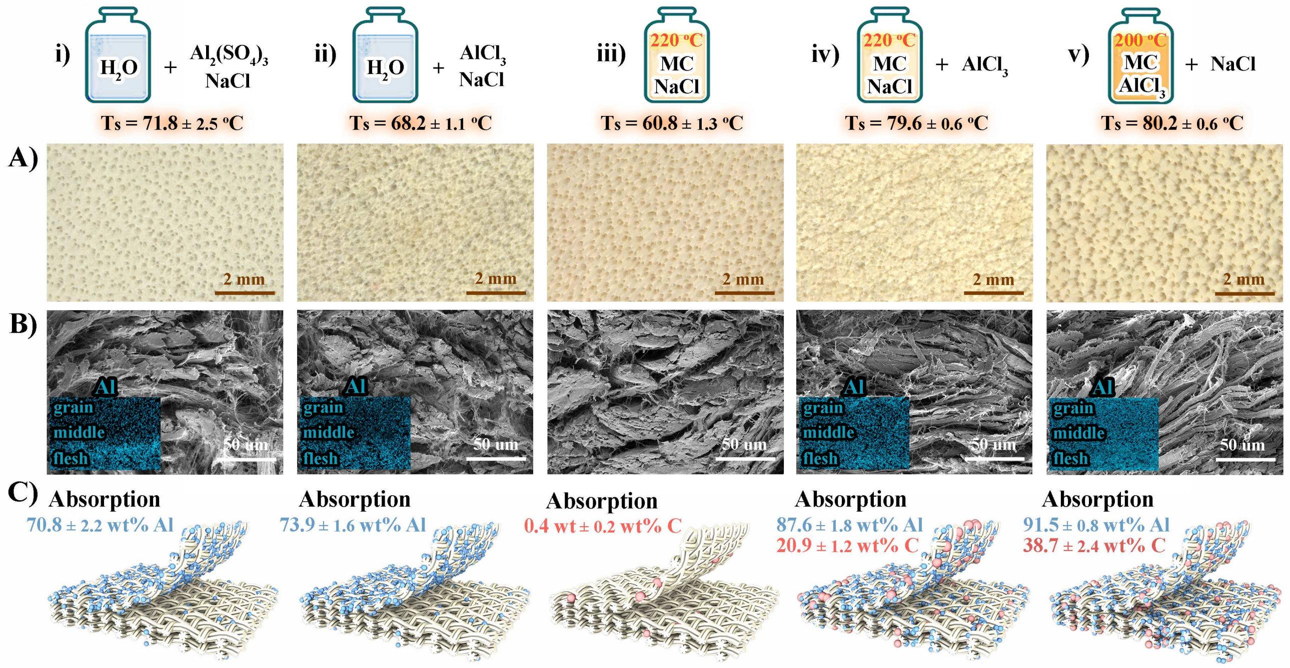

Fig. 2 A) Stereo microscope images of grain surface; B) SEM and Al mapping images of the cross section and C) distribution of Al and C elements in leathers tanned by different tanning agents.

tanning agent. Concentrated NaCl aqueous solutions lower the solubility in water of THF and the generated products, which allows the formation of a biphasic NaCl-H_2O/THF solvent system, thus improving the extraction efficiency. With this procedure some components of the tanning agent can spontaneously dissolve in the H_2O or THF phase depending on their solubility.[16, 24] In particular, approximately 80% of furans (including 5-hydroxymethylfurfural and furfural) and 60% of carboxylic acids (including formic, acetic, lactic and levulinic acids) were successfully extracted as valuable chemicals from the tanning solution (aqueous phase) to the THF phase. This procedure resulted in a remarkable decrease in the ΔE value of the tanned leather. In addition, it must be borne in mind that the NaCl solution used in this extraction system can be directly employed in the tanning process, as NaCl prevents picked cattle skin from swelling. Thus, this extraction procedure can be regarded as a green procedure, where NaCl can be further utilized and THF can be efficiently recovered, with only minimal losses largely accounted for by its small solubility in water. In addition, the high molecular weight oligosaccharides might be converted into different value-added products to improve the sustainability and green nature of the process; although, prior to their subsequent conversion, further work need to be conducted on the analysis of how and to what extent these species are modified during our treatment. Noticeably, the extraction procedure used to purify the tanning agent increased up to 4.5 °C of T_s for the tanned leather (Fig. 1A). It has been widely reported that $[Al(OH)_1(aq)]^{2+}$ and $[Al(OH)_2(aq)]^{+}$ are the most common species co-existing in $AlCl_3$ aqueous solutions,[25, 26] which can coordinate with the active groups of the oligosaccharides and collagen fibers. Furthermore, this extraction process also promotes the removal of the oligomers with molecular weight higher than 5000 g/mol and, as a result, the average molecular weight of the oligosaccharides in the tanning agent was reduced by half. This is very important to increase the efficiency of this tanning solution as lowering the molecular weight of the oligosaccharides enhances the penetration of the 'Al-oligosaccharide complex' into the leather. In addition, this also produces a greater spread of the coordination reactions of the Al species in the hierarchical structure of the collagen fiber, thus increasing the thermal stability of the tanned leather.[27]

To study the influence of the molecular size distribution of the oligosaccharides on the tanning efficiency, a series of cellulose-derived tanning agents were prepared under different reaction conditions (Fig. S1 to S3). Increasing the cellulose concentration (starting material) to 6 wt% led to an increase in the proportion of high molecular weight Al-oligosaccharide complexes (>5000 g/mol). This hindered the penetration of Al species into the skin matrix, which led to a pronounced decrease in the T_s of the tanned leather. [28] Although the hierarchical structure of the collagen fibers provides the material with a broad pore and channels inner diameter distribution (5 nm to 120 µm), [29] the oligosaccharides with a particle size greater than 15 nm (over 5000 g/mol, >30 glucose repeating units) are incapable of carrying Al into the primary collagen fibers, thus hampering further crosslinking reactions to take place. Besides, the weak tanning properties of the diluted oligosaccharide solution (0.5 wt% cellulose concentration) also provided evidence for the central effect of the cellulose-degraded oligosaccharides during Al tanning.

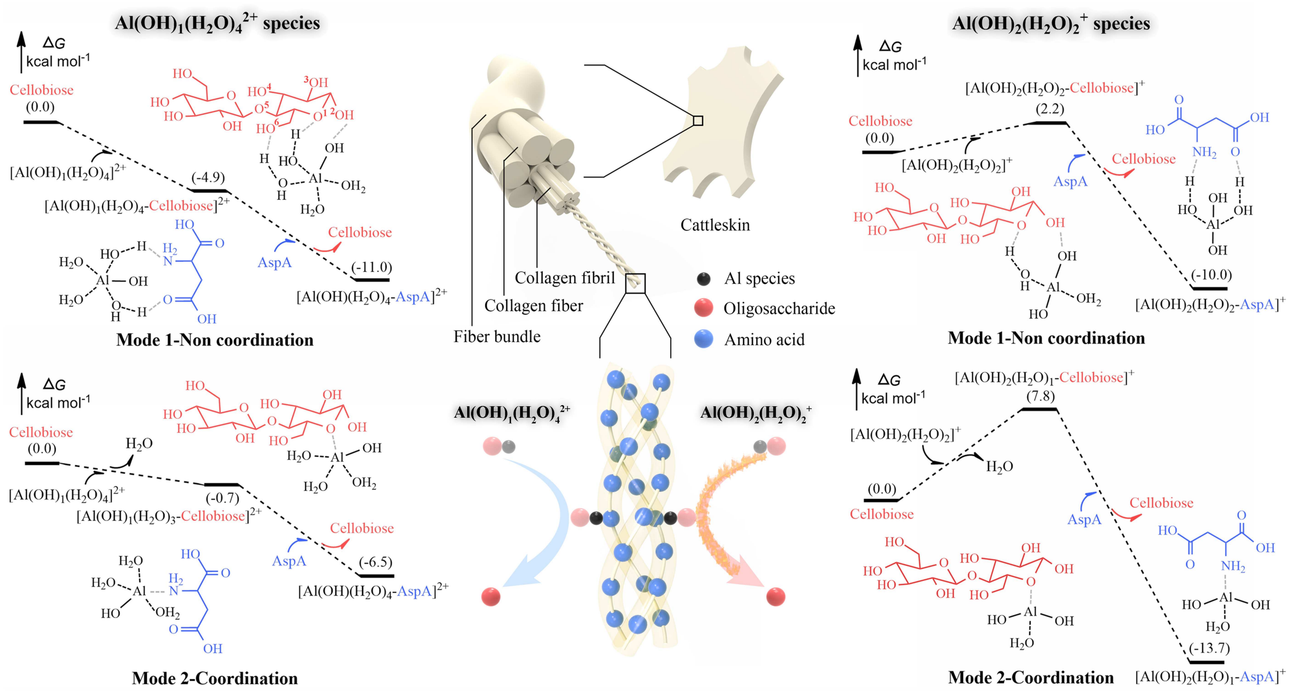

Fig. 3 Energy profiles for the interactions of cellobiose and aspartic acid (AspA) with the active Al species.

In the light of the above results, control experiments were conducted to reveal the effects of the Al species and cellulose-derived oligosaccharides on the tanning process (Fig. 2). In the absence of oligosaccharides, the T_s of the leather tanned by an $Al_2(SO_4)_3$ solution (**i**) or an $AlCl_3$ solution (**ii**) was only around 70 ºC, which indicates that these two tanning agents have a low tanning efficiency. From the stereo microscope images taken, it was observed that this oligosaccharide-free Al-tanned leather had a relatively coarse grain surface, especially the material treated with the $AlCl_3$ solution, probably due to the accumulation of Al species on the leather surface. In particular, the poor absorption performance of Al in the tanning process, the low dispersion degree in the cross section of the collagen fibers and the intensive accumulation of Al on the flesh side of the tanned leather, reveal the ineffective tanning properties of these two 'oligosaccharides-free' tanning agents. This undesirable penetration behavior is closely related to the low T_s of the tanned leather. As NaCl was reported to promote the conversion of cellulose, [19, 21, 24] a reaction liquid produced from the NaCl-assisted cellulose degradation was prepared in the absence of $AlCl_3$. Not surprisingly, the T_s was as low as 60.8 ºC and a substantial agglomeration of the collagen fibers was observed when using this Al-free hydrolysate as the tanning agent (**iii**), thus confirming the limited tanning effect of the oligosaccharides on their own.

Then, the tanning properties of two more hydrolysates were compared. This includes the aforementioned NaCl-induced oligosaccharides plus additional $AlCl_3$ (**iv**), and the $AlCl_3$-induced oligosaccharides (**v**). The experimental results revealed that both oligosaccharides-containing solutions showed an exceptional tanning performance with a T_s of leather close to 80 ºC. Therefore, this Al-oligosaccharides complex produced by $AlCl_3$-catalyzed cellulose depolymerization can be regarded as a potential tanning agent for the leather industry. However, the tanning agent **v** presented a slightly better tanning efficiency than the agent **iv**. For instance, smoother grain and clearer pores could be observed for the leather tanned with the solution **v**. A higher dispersion of the collagen fibers together with a more uniform distribution of Al in the grain, middle and flesh sides indicate a more efficient penetration and dispersion of Al in leather when using the solution **v**. The GPC analysis revealed that the molecular weight of the oligosaccharides produced using the NaCl-H_2O reaction system was much higher than those produced with the $AlCl_3$-H_2O reaction system. Therefore, Al-oligosaccharides complexes with a large particle size will block the channel, hindering their penetration into skin matrix, thus lowering the absorption of Al and organics on the leather. Besides, Al can coordinate differently with the oligosaccharides when increasing the temperature, leading to a different penetration behavior of Al into the skin matrix.

In order to gain a deep insight into the reaction mechanism of the masking effect that the cellulose-degraded oligosaccharides exert on Al penetration, as well as on its further coordination with the collagen fibers, computational simulations were conducted. For these theoretical computation experiments, cellobiose and aspartic acid (AspA) were selected as the model compounds for cellulose and collagen fibers, respectively (Fig. 3). In addition, $[Al(OH)_1(aq)]^{2+}$ and $[Al(OH)_2(aq)]^{+}$ were chosen as the active Al species in the $AlCl_3$ aqueous solution according to the literature. [25, 26] Due to the low electronegativity of the oxygen in polyhydroxy cellobiose and, consequently, the low coordination ability of cellobiose with Al species, two types of Al-interaction were simulated; i.e. a non-coordination mode (by hydrogen bonds) and a coordination

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mode. At room temperature, $[Al(OH)_1(H_2O)_4]^{2+}$ species can easily interact with O-1, O-2 and O-6 of cellobiose by three hydrogen bonds (ΔG=-4.9 kcal mol^{-1}), while they can also spontaneously coordinate with O-1 of cellobiose (ΔG=-0.7 kcal mol^{-1}). With the addition of AspA, the coordination between cellobiose and the $[Al(OH)_1(H_2O)_4]^{2+}$ species does not take place. Instead, AspA generates a hydrogen bonding network (at $-NH_2$ and –COOH groups) or coordinates (at $-NH_2$ group) with $[Al(OH)_1(H_2O)_4]^{2+}$ species, with ΔG of -6.1 and -5.8 kcal mol^{-1}, respectively. This demonstrates the masking effect of the oligosaccharides by means of a first weak interaction/coordination with the $[Al(OH)_1(H_2O)_4]^{2+}$ species, followed by a stronger crosslinking reaction of the Al species with the collagen fibers. Similar to $[Al(OH)_1(H_2O)_4]^{2+}$ species, AspA can also replace the cellobiose molecule on $[Al(OH)_2(H_2O)_n\text{-cellobiose})]^+$ complex according to the negative ΔG obtained for this reaction. However, the formation of the hydrogen bonding network and the coordination of $[Al(OH)_2(H_2O)_2]^+$ species with cellobiose have an energy barrier of 2.2 and 7.8 kcal mol^{-1}, respectively. Thus, additional energy (such as heating) is required for the oligosaccharides to be able to act as a masking ligand for the Al species. This explains very well the greater Al penetration of the solution **v** than that of the solution **iv**, in which oligosaccharides can in situ interact and/or coordinate with either $[Al(OH)_1(H_2O)_4]^{2+}$ or $[Al(OH)_2(H_2O)_2]^+$ due to the higher reaction temperature achieve in the solution **v**.

Conclusion

In this paper, the dual-function of $AlCl_3$ was explored and fully utilized via the development of a ‘Trojan Horse Strategy’; i.e. $AlCl_3$ was used to efficiently catalyze cellulose depolymerization into oligosaccharides as well as to produce a water soluble ‘Al-oligosaccharides’ complex that can be used as an environmentally friendly tanning agent. Our results revealed that the oligosaccharides produced during cellulose depolymerization were able to interact/coordinate with the Al species first, preventing to a large extent the over crosslinking reaction of Al species on the leather surface, which efficiently boosted the subsequent penetration of Al into the leather. Then, the coordinated Al species were released from the Al-oligosaccharide complex and strongly interacted/coordinated with the amino groups of the collagen fibers. This two-step procedure aided the dispersion and stabilized the fiber bundles so as to improve the leather properties. Therefore, the mechanistic understanding of this novel oligosaccharides-assisted tanning process reported in this work provides very useful insights into the development of renewable-based tanning agents, which may substantially contribute towards the sustainable development of the leather industry.

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Conflicts of interest

There are no conflicts to declare.

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