

12th Asia International Conference On Leather Science And Technology

Views on the design of sustainable chrome-free tanning agent

Dr. Wang Ya-nan

Sichuan University

Oct.19, 2022 in Palmerston North, NZ

Main Contents

- ◆ **Background: the demand for Cr-free tanning**
- ◆ **Our Cr-free tanning technologies**
- ◆ **Design of Cr-free tanning agent: Biodegradation**
- ◆ **Design of Cr-free tanning agent: Size**
- ◆ **Design of Cr-free tanning agent: Charge**



1. Background: the demand for Cr-free tanning

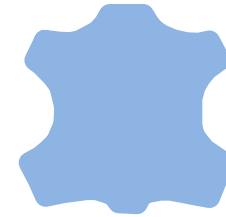
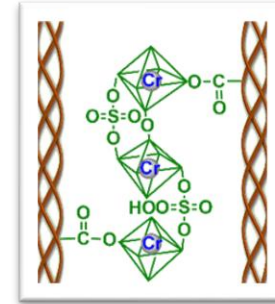


Raw hide



Cr(III) salts

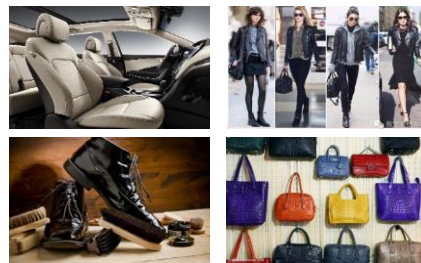
Tanning



Leather



Cr-tanned leather



Diverse leather goods



Cr-containing wastewater



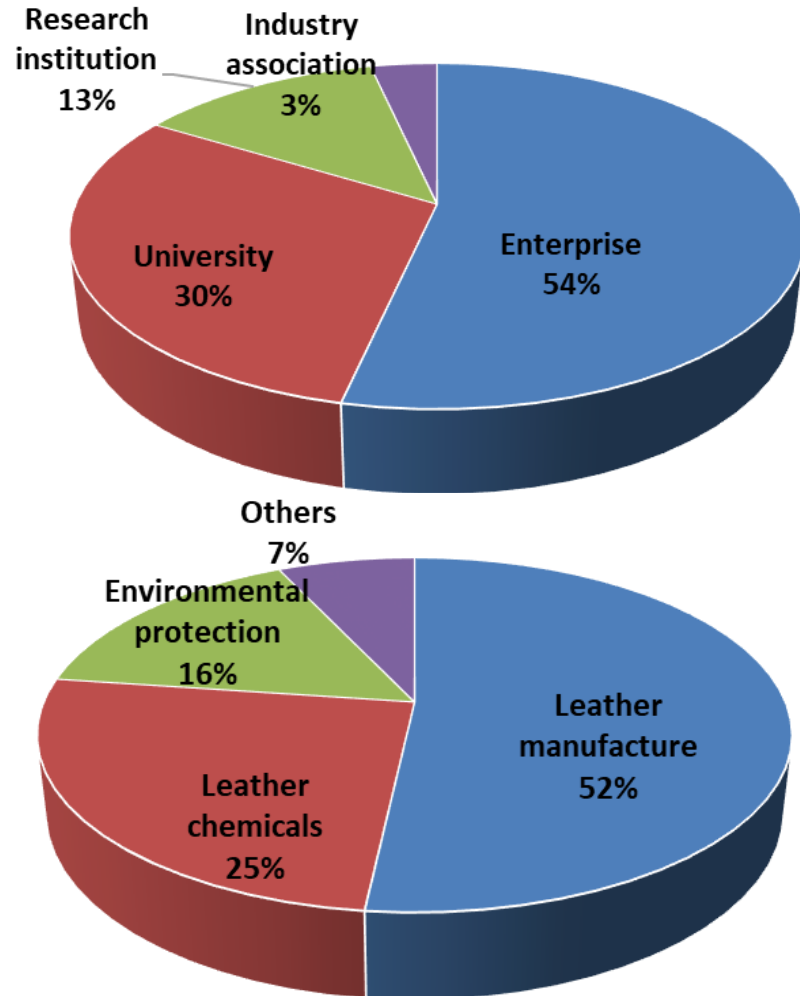
Cr-containing solid waste

- ✓ Proper tanning performance
- ✓ Excellent properties of leather
- ✓ Versatility and popularity

- ✗ Potential environmental risk
- ✗ Strict policies on Cr emission in China
- ✗ Limiting development of leather industry

1. Background: the demand for Cr-free tanning

A survey of the technology roadmap in China leather industry, 2022 (86 questionnaires)



Technology	Significance index
Utilization of Cr-containing leather solid waste	91.47
Cr reduction process	91.27
Utilization of Cr-containing sludge	90.96
Water-saving technology	88.39
Cr-free tanning process	87.35
Cr-free tanning agents	85.98
Eco-friendly dyestuff	84.04
Waterborne finishing agents	83.73
...	...

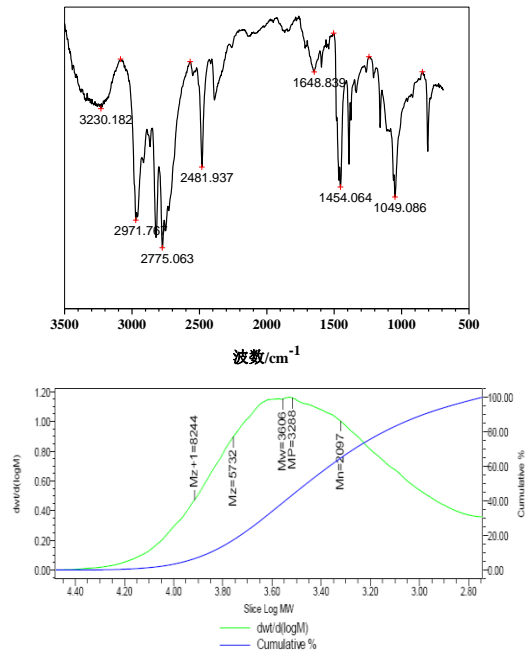
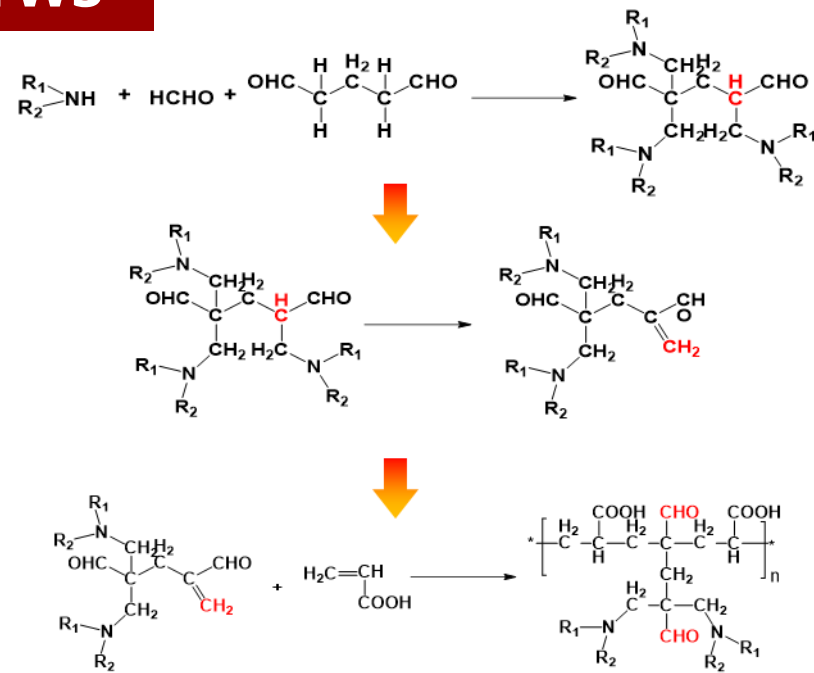
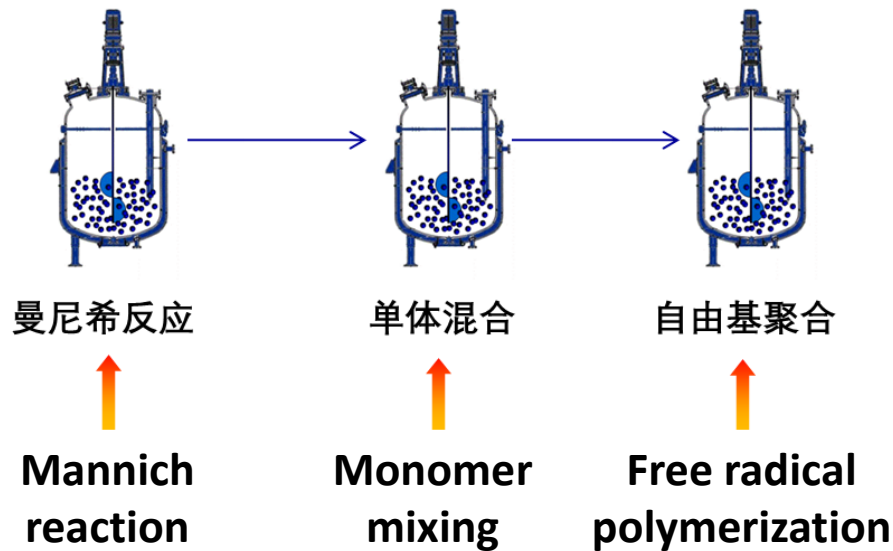
Main Contents

- ◆ Background: the demand for Cr-free tanning
- ◆ **Our Cr-free tanning technologies**
- ◆ Design of Cr-free tanning agent: Biodegradation
- ◆ Design of Cr-free tanning agent: Size
- ◆ Design of Cr-free tanning agent: Charge



2. Our Cr-free tanning technologies

Amphoteric organic tanning agent: TWS



Molecular weight 2000



TWS production line

Low toxicity, non-irritating and weak sensitizing effects
BOD₅/COD>0.30, biodegradable



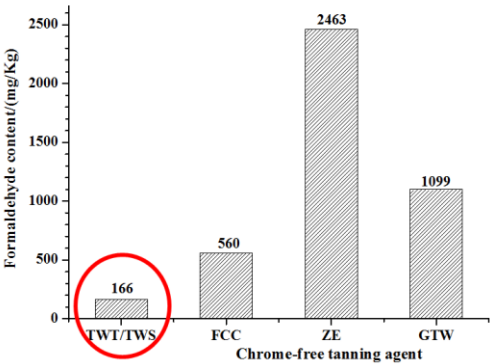
Test reports

2. Our Cr-free tanning technologies

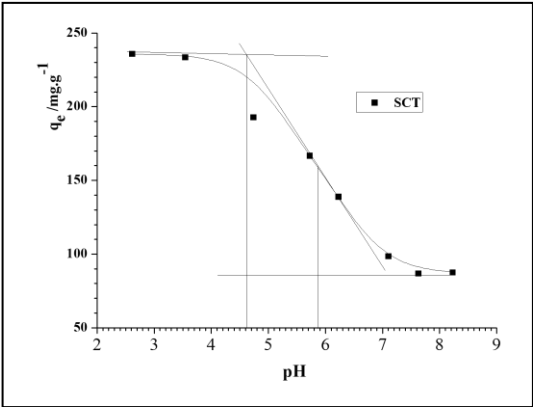
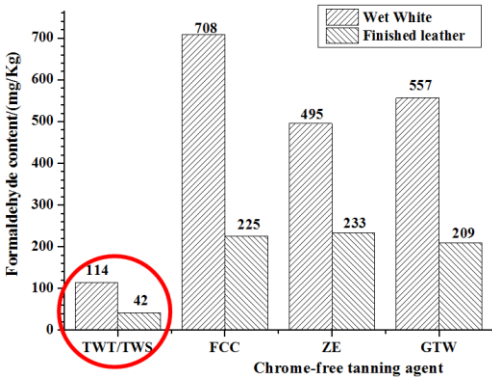
Amphoteric organic tanning agent: TWS

Tanning agent	TWS	Organophosphine	Active chlorine	Modified glutaraldehyde
Ts of wet white/ °C	~90	86	70~75	85
Ts of finished leather / °C	>85	83	80	82
Dosage	4%~6%	4%~6%	10%	4%~6%

Formaldehyde in wastewater



Formaldehyde in leather



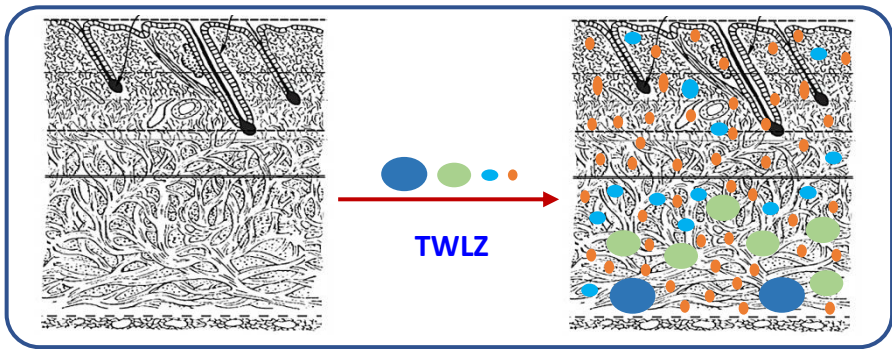
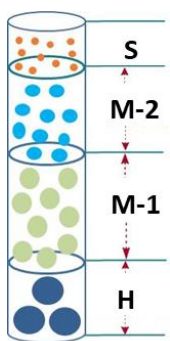
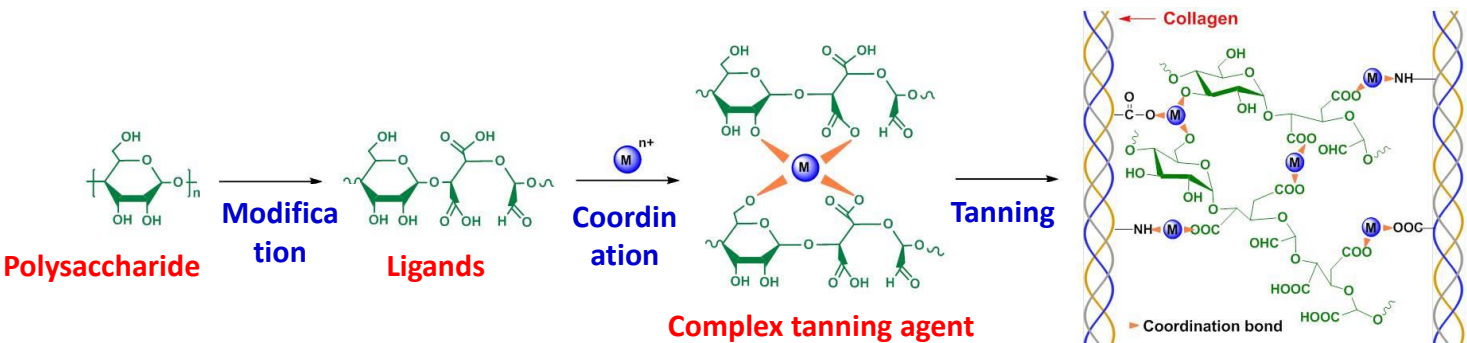
High IEP of TWS wet white

Tanning agent	TWS	Organophosphine	Modified GA
Uptake of fatliquors/%	99	88	82
Uptake of dyestuff/%	95	88	78

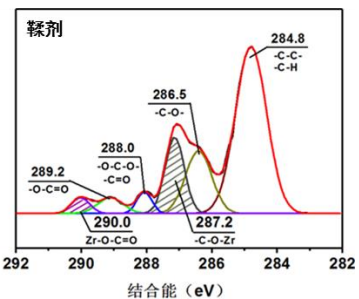
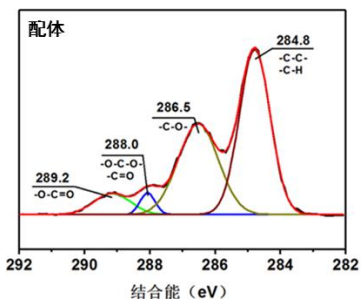
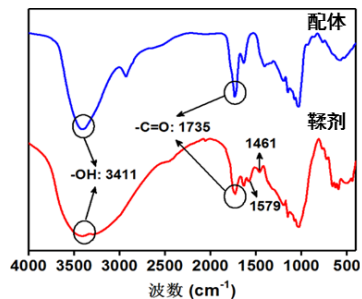
High Ts (~90°C)
Extremely low
formaldehyde content

2. Our Cr-free tanning technologies

Complex tanning agent: TWLZ



Wide distribution
for penetration



Multiple groups
for fixation



TWLZ production line



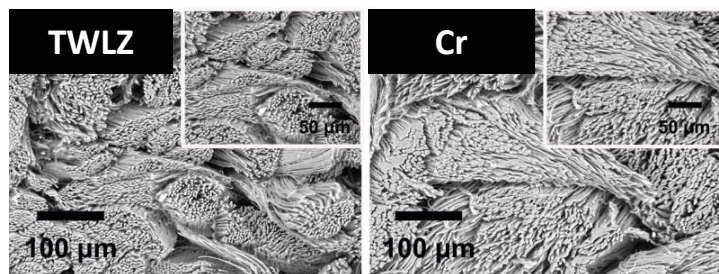
TWLZ patents and test reports

2. Our Cr-free tanning technologies

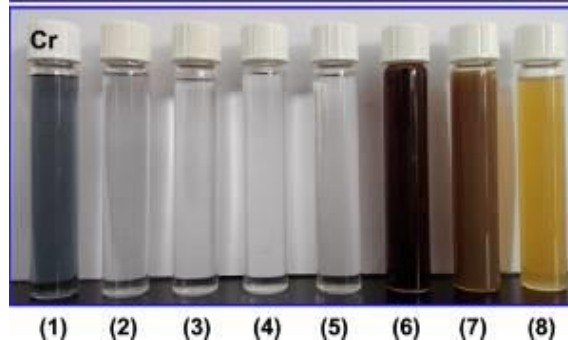
Complex tanning agent: TWLZ

Tanning conditions: TWLZ dosage 7%~8%, penetration duration 3~5 h, fixing temperature 38~40°C, final pH 4.0~4.2

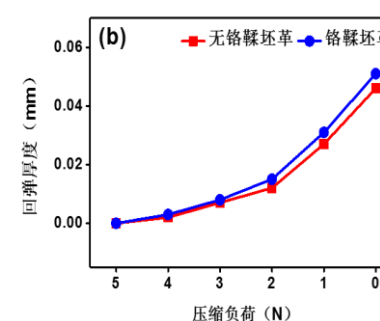
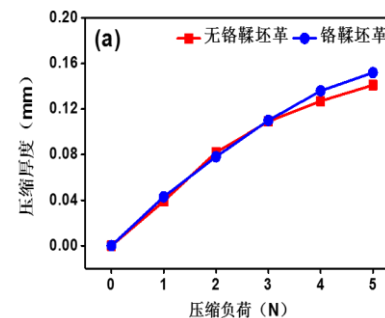
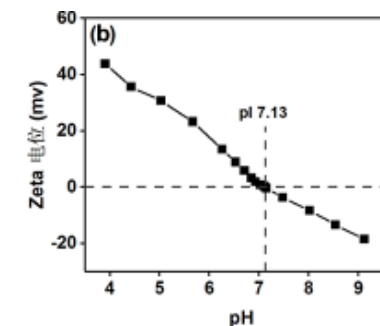
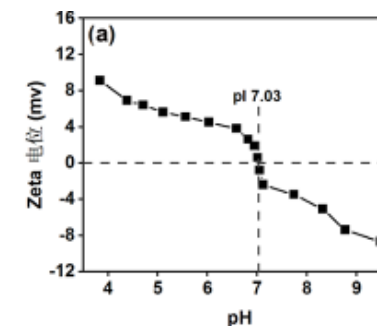
Even distribution of TWLZ, uptake rate 95%, $T_s > 85^\circ\text{C}$



Fiber dispersion of crust leather



Uptake of post-tanning chemicals

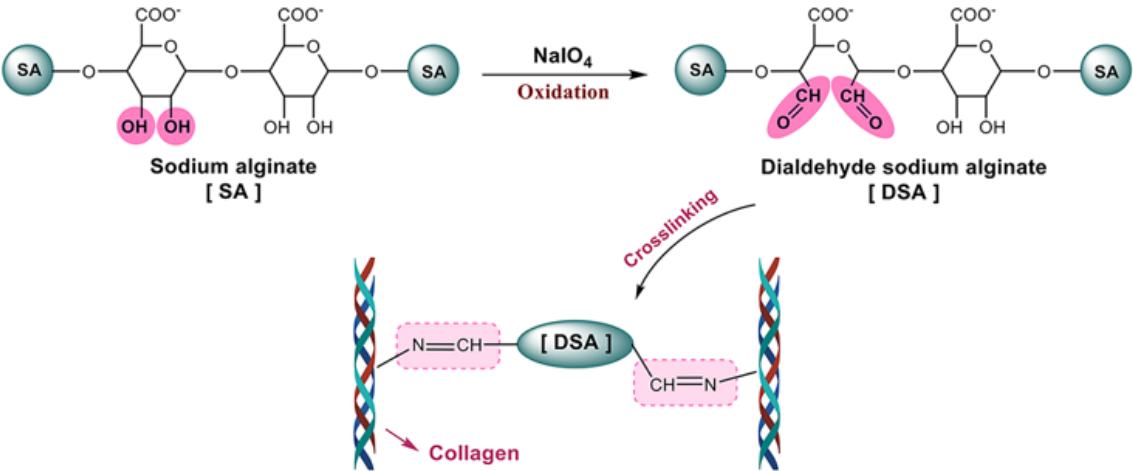


Similar IEP and organoleptic properties with Cr tanned leather

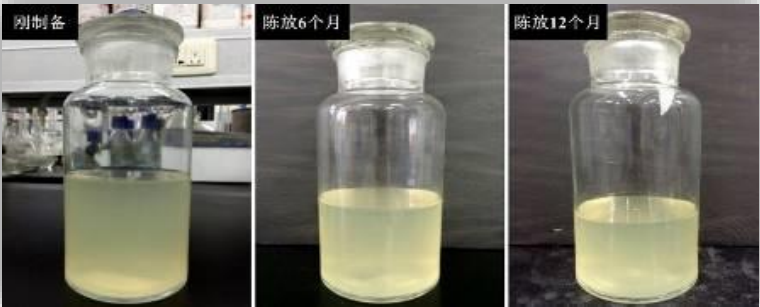
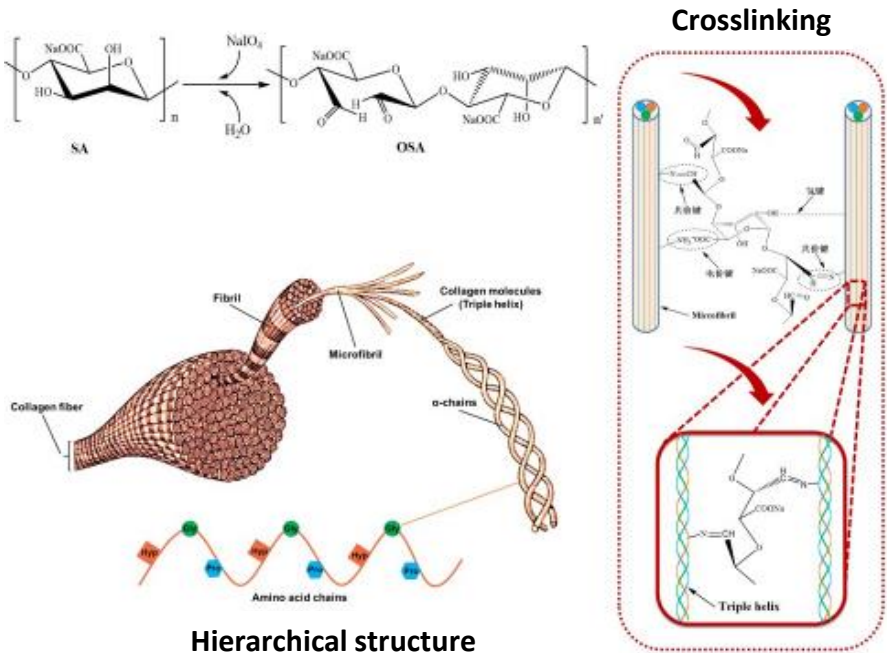
2. Our Cr-free tanning technologies

Dialdehyde polysaccharide tanning agent: OSA

Periodate oxidation



Tanning mechanism of OSA



OSA: Cr, formaldehyde and metal-free



OSA: Patents



OSA: Test reports

2. Our Cr-free tanning technologies

Application of Cr-free tanning technologies



Application range

Cr-free main tanning

Cr-free retanning

Cr-free pretanning

The Cr-free tanning agents have been used in upper leather, sofa leather, garment leather, car seat leather and fur production



Main Contents

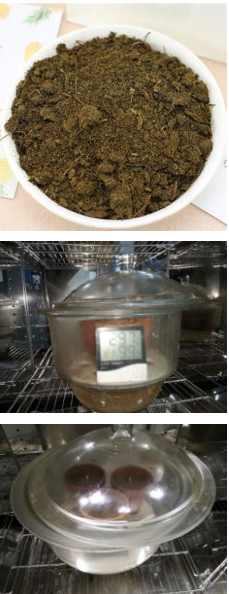
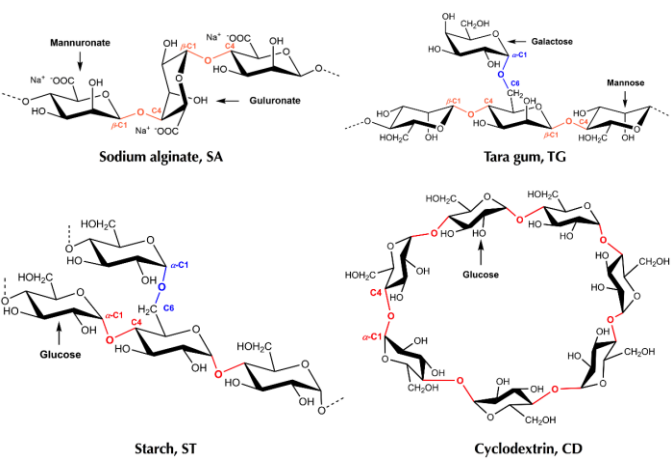
- ◆ Background: the demand for Cr-free tanning
- ◆ Our Cr-free tanning technologies
- ◆ **Design of Cr-free tanning agent: Biodegradation**
- ◆ Design of Cr-free tanning agent: Size
- ◆ Design of Cr-free tanning agent: Charge



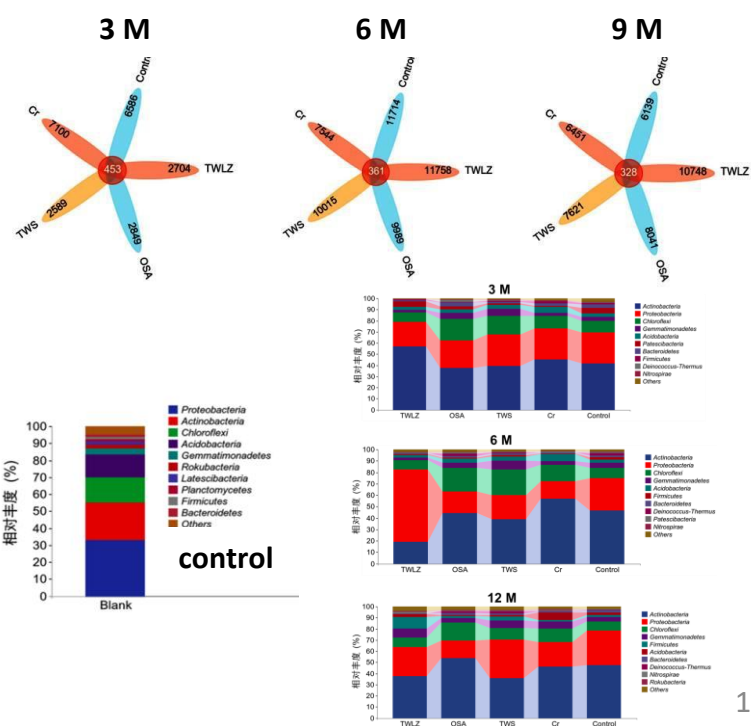
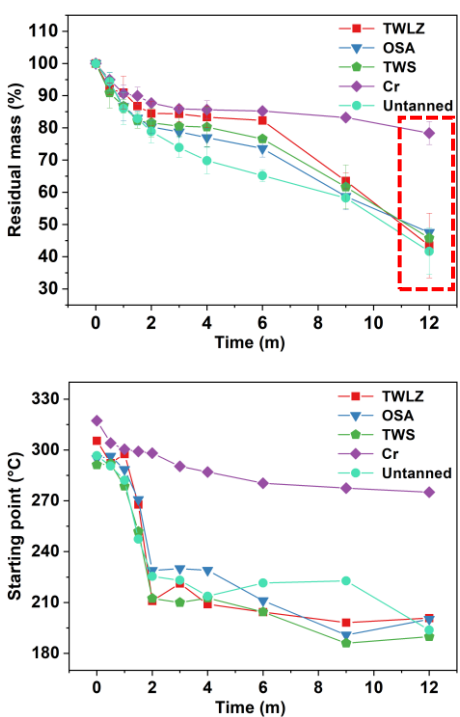
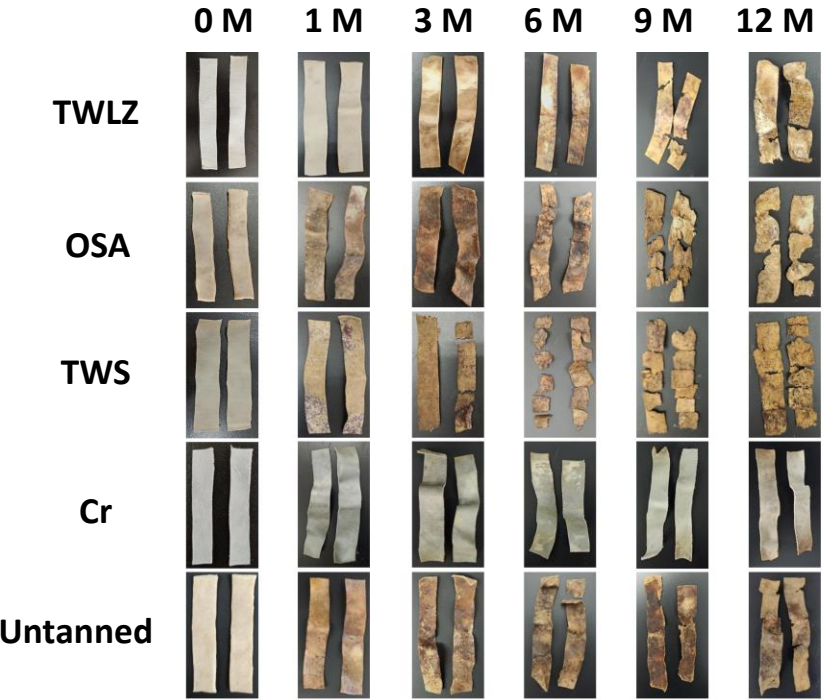
3. Design of Cr-free tanning agent: Biodegradation

Biomass tanning agent

- Polysaccharide: low-carbon raw material
- Repeat unit and rich functional groups
- eco-friendly and sustainable



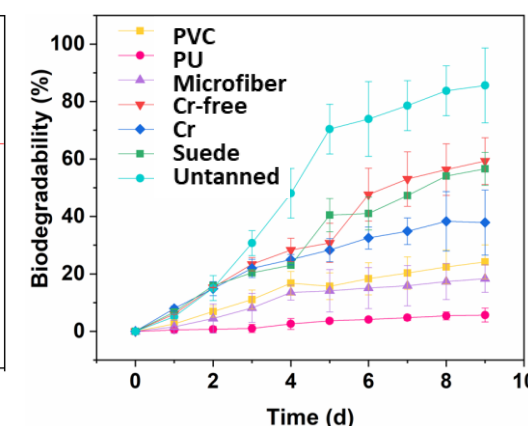
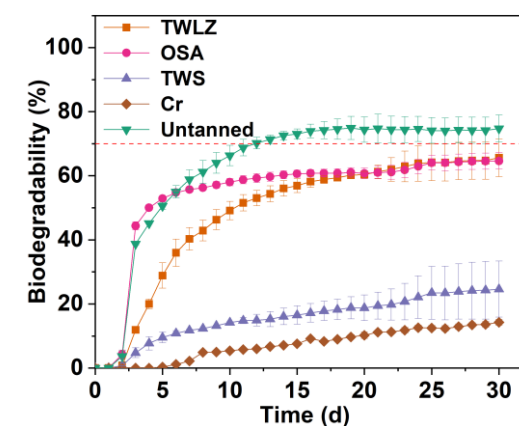
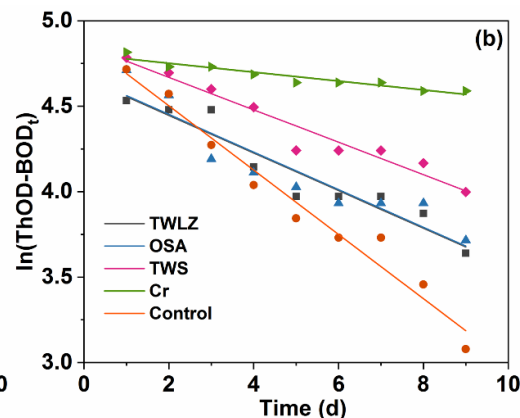
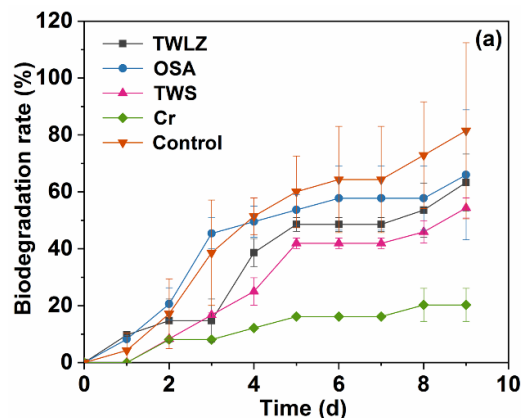
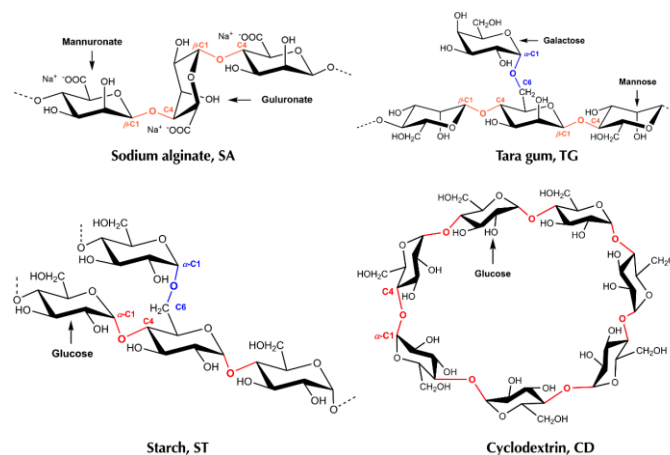
Soil burial test of leather



3. Design of Cr-free tanning agent: Biodegradation

Biomass tanning agent

- Polysaccharide: low-carbon raw material
- Repeat unit and rich functional groups
- eco-friendly and sustainable



Biodegradation of leather in aqueous medium

Biodegradation of tanned leather
BOD test GB/T 19276.1

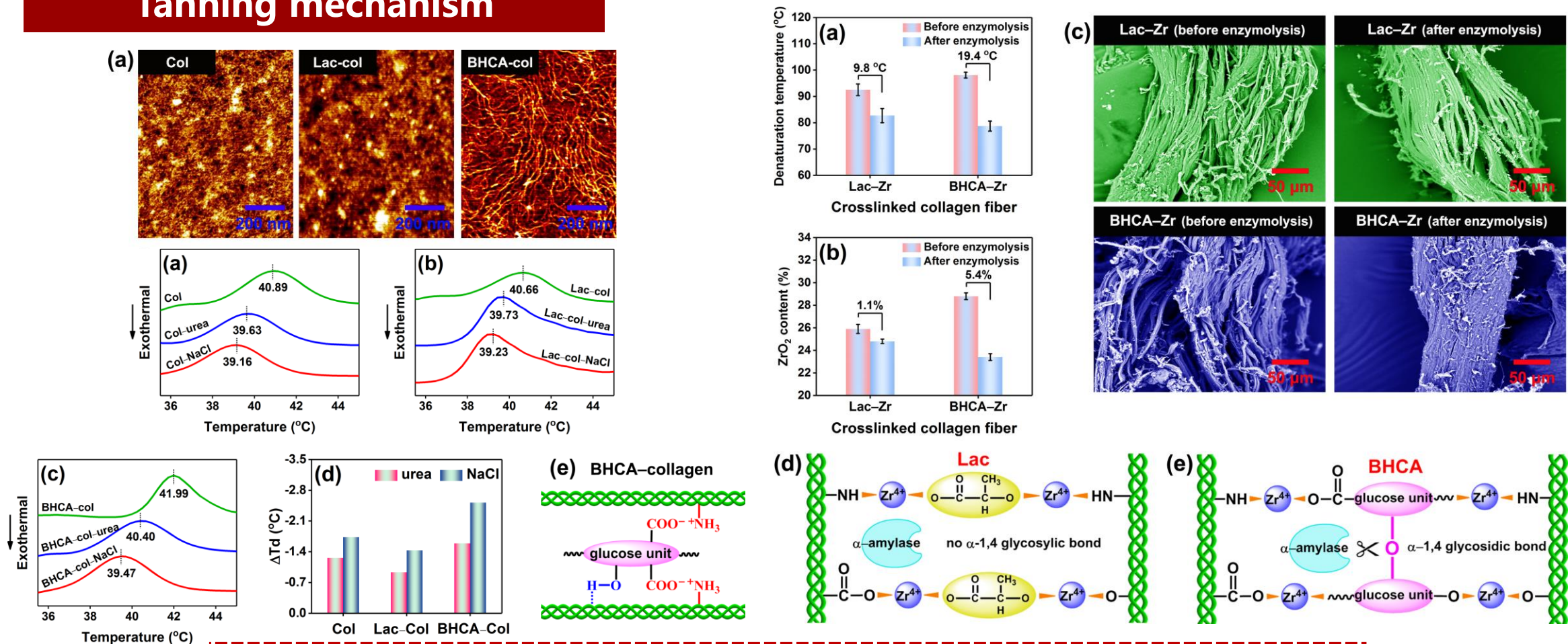
Biodegradation of tanned leather
Evolved CO₂ test ISO 20136

Leather vs. Synthetic materials

Biodegradation: Leather >> Synthetic materials,
Biomass tanned leather > Other Cr-free leather >> Cr leather

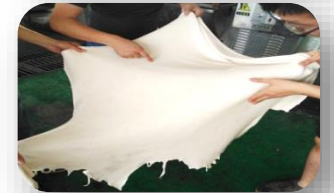
3. Design of Cr-free tanning agent: Biodegradation

Tanning mechanism



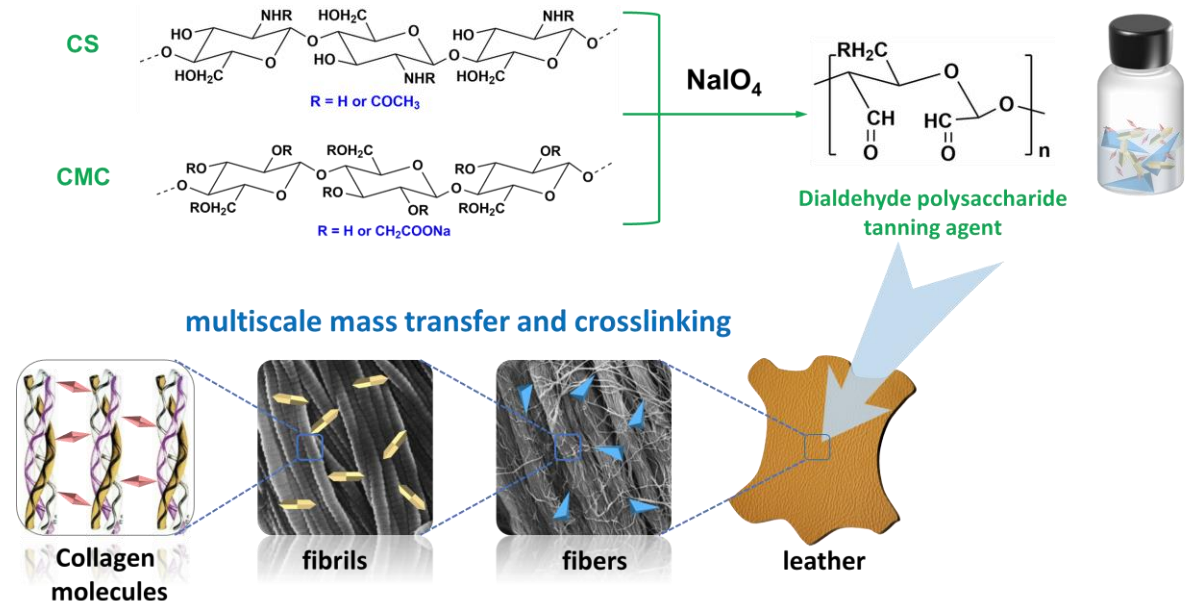
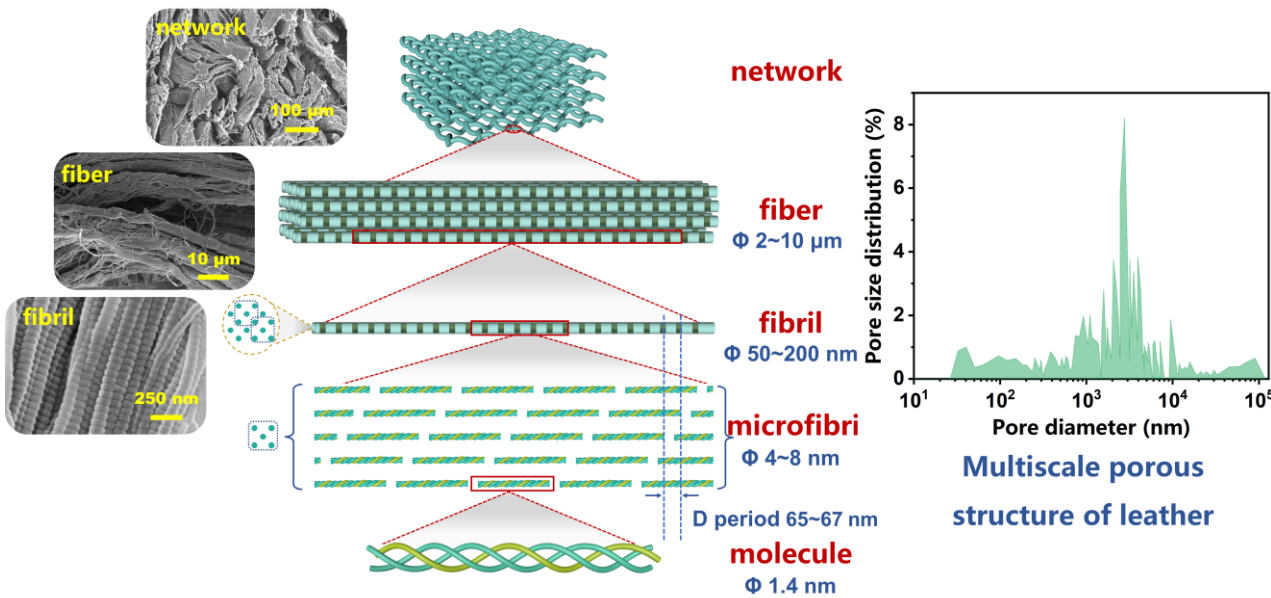
Main Contents

- ◆ Background: the demand for Cr-free tanning
- ◆ Our Cr-free tanning technologies
- ◆ Design of Cr-free tanning agent: Biodegradation
- ◆ Design of Cr-free tanning agent: Size
- ◆ Design of Cr-free tanning agent: Charge



4. Design of Cr-free tanning agent: Size

Key issue: regulation of tanning agent structure → control of multiscale mass transfer and crosslinking
→ evolution of leather hierarchical structure → exhibition of tanning effects



Why use dialdehyde polysaccharide tanning agent as the model?

- The products have multiple aldehyde groups to crosslink with collagen.
- The size of products can be varied due to the repeat units of polysaccharide.
- The charge of products can be adjusted by polysaccharide selection.

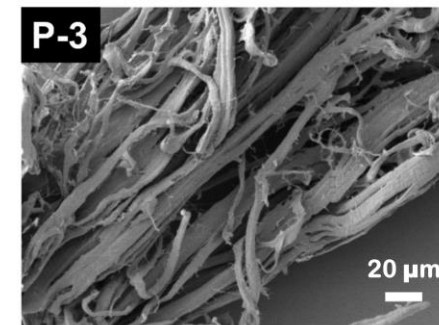
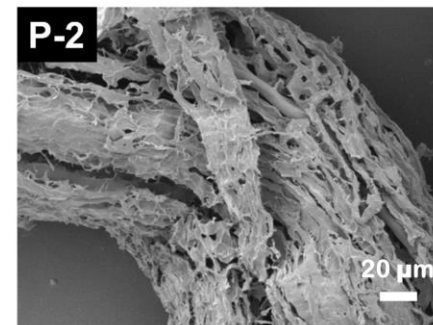
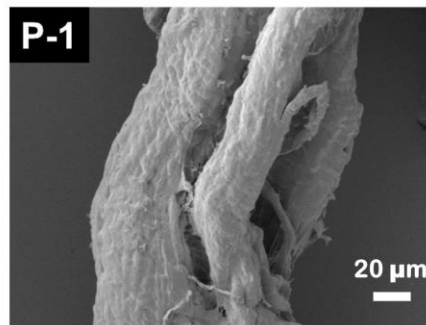
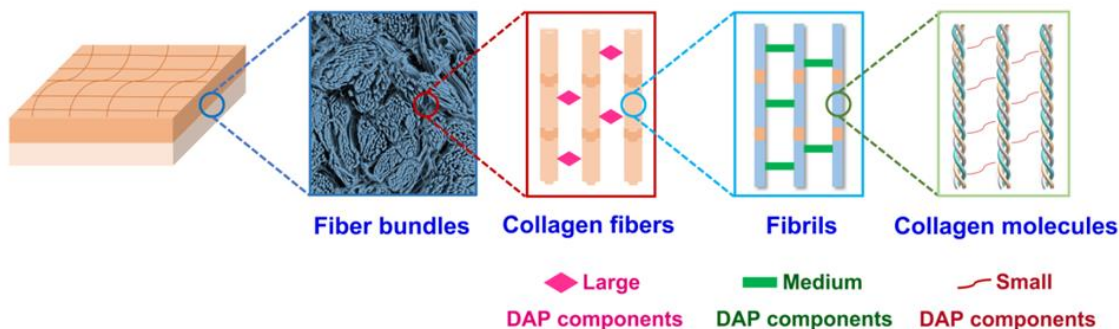
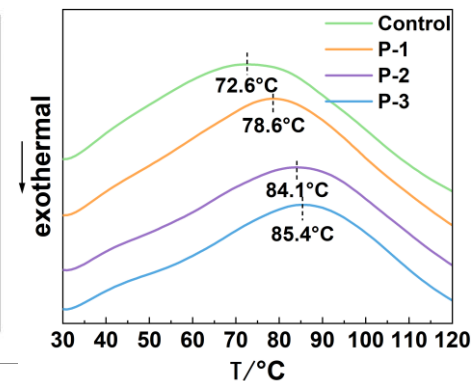
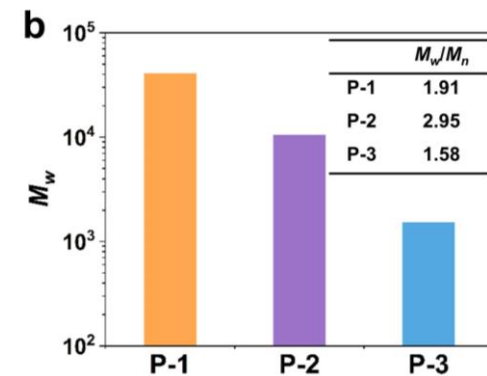
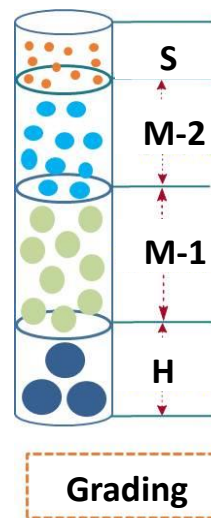
4. Design of Cr-free tanning agent: Size

Multiscale mass transfer and crosslinking of tanning agent

Size regulation of tanning agent



Crosslinking in different layers

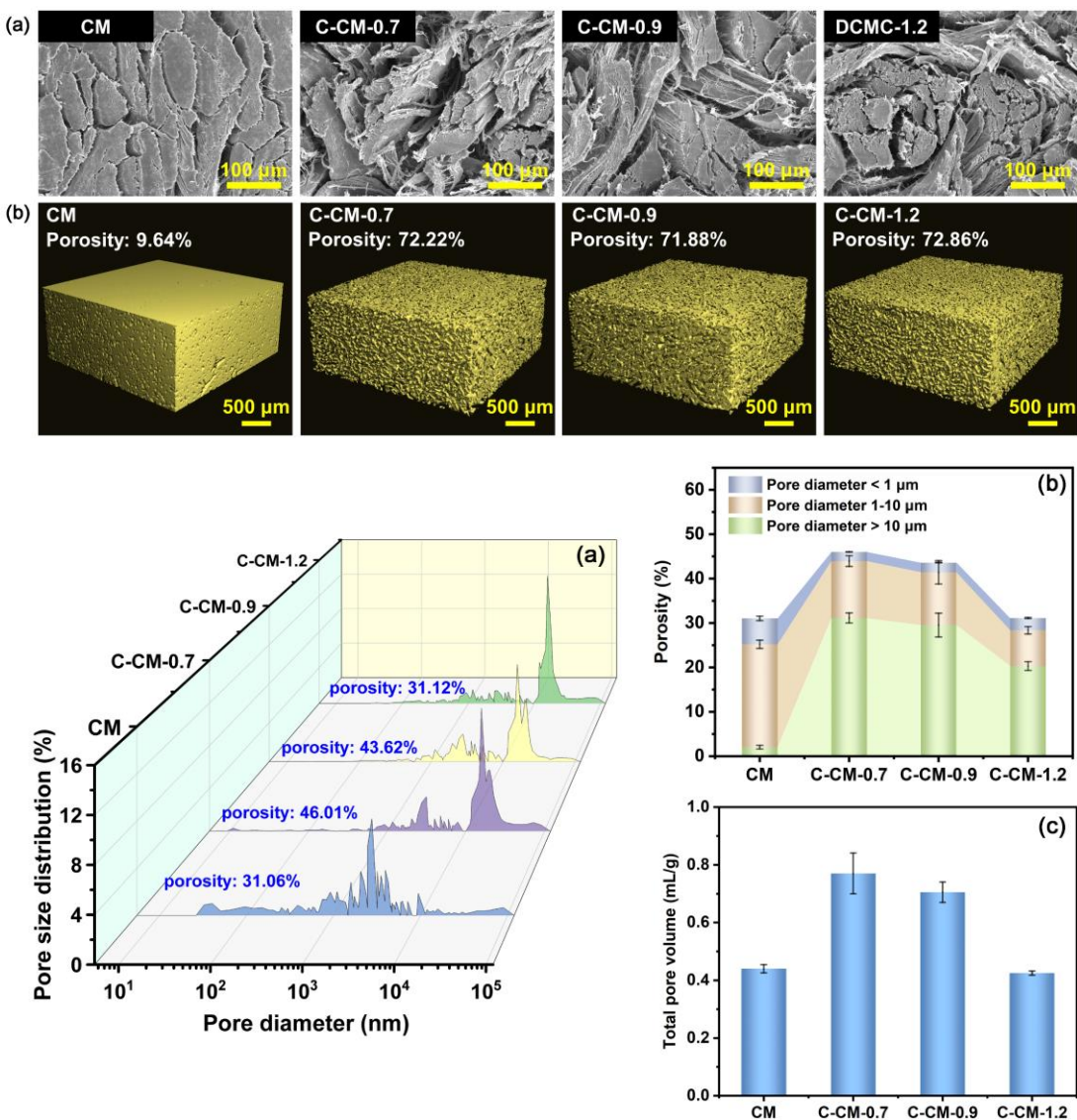
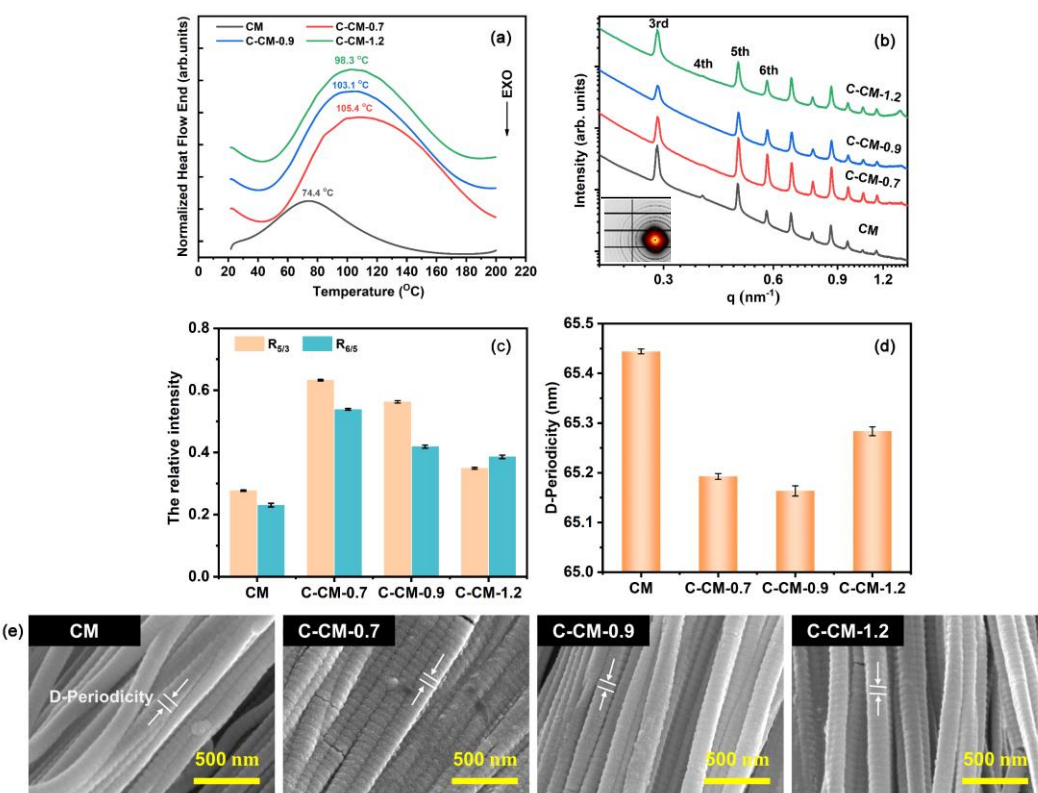


Relationship between size of tanning agent and tanning effects

4. Design of Cr-free tanning agent: Size

Multiscale mass transfer and crosslinking of tanning agent

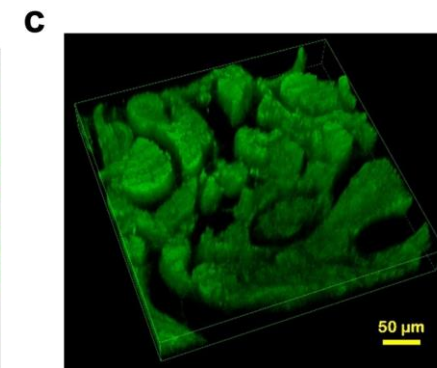
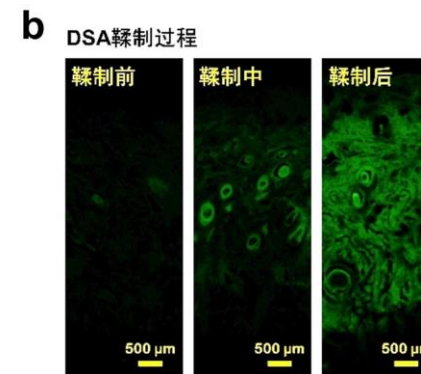
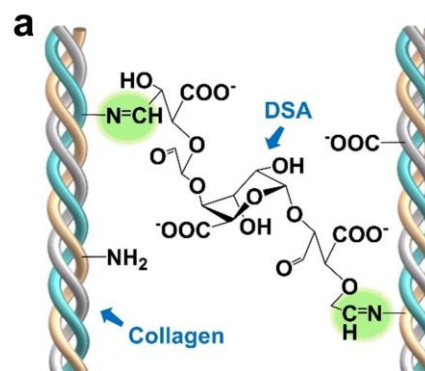
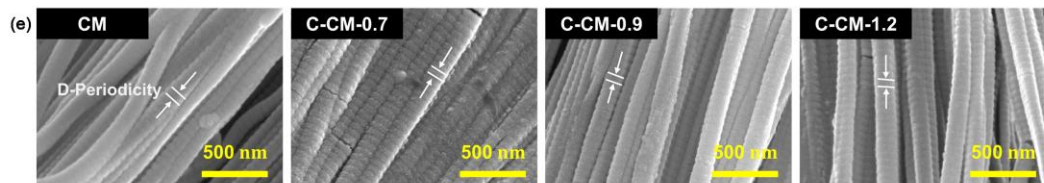
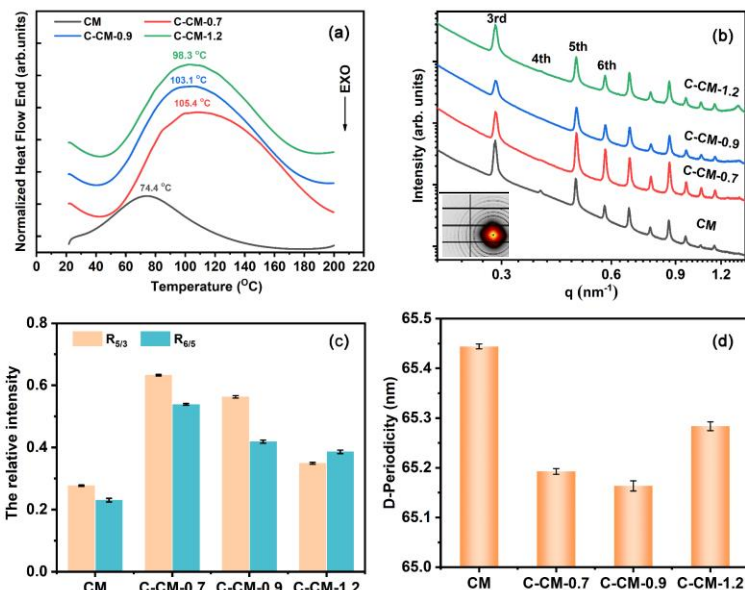
Evolution of hierarchical structure by tanning



4. Design of Cr-free tanning agent: Size

Multiscale mass transfer and
crosslinking of tanning agent

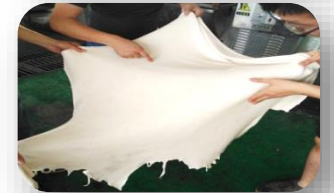
Evolution of hierarchical
structure by tanning



- Revealing tanning mechanism
- Guiding the design and development of Cr-free tanning agent

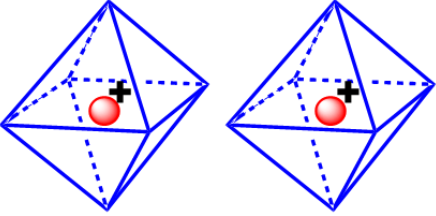
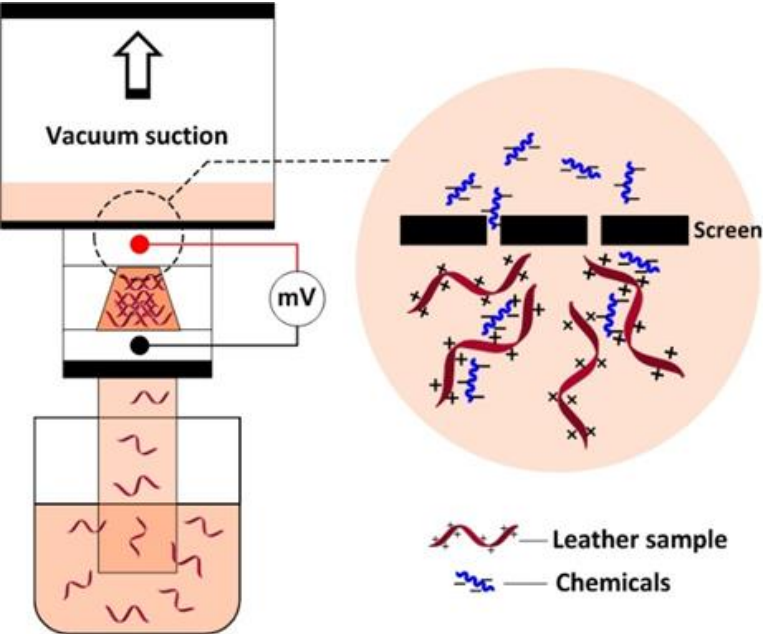
Main Contents

- ◆ Background: the demand for Cr-free tanning
- ◆ Our Cr-free tanning technologies
- ◆ Design of Cr-free tanning agent: Biodegradation
- ◆ Design of Cr-free tanning agent: Size
- ◆ Design of Cr-free tanning agent: Charge

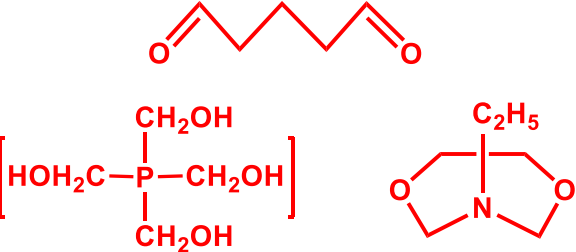


5. Design of Cr-free tanning agent: Charge

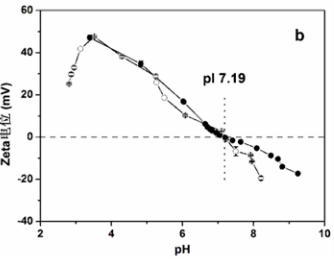
Leather: zwitterionic property
Tanning agent: charged groups/reacting with collagen



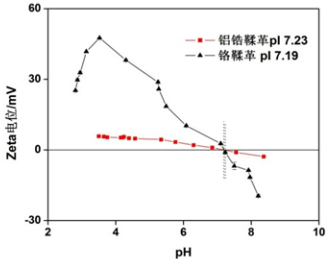
Cr tanning agent
Reacting with carboxyl



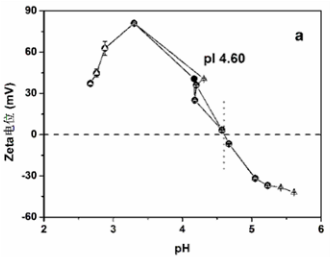
Aldehyde
Reacting with amino



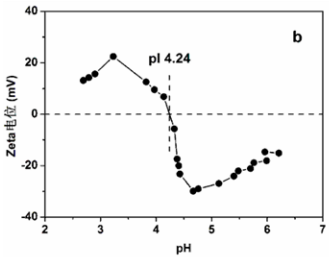
Cr: pI 7.2



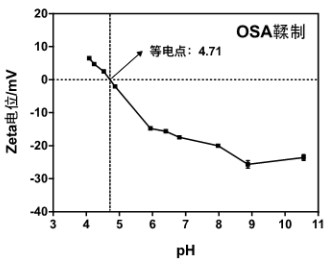
TWLZ: pI 7.2



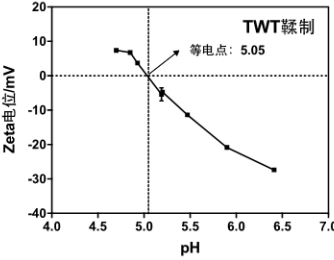
Vegetable: pI 4.6



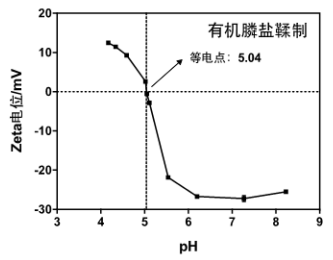
Syntan: pI 4.2



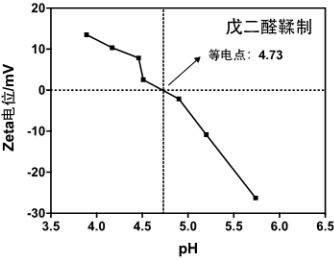
OSA: pI 4.7



TWS: pI 5.1



OP: pI 5.0

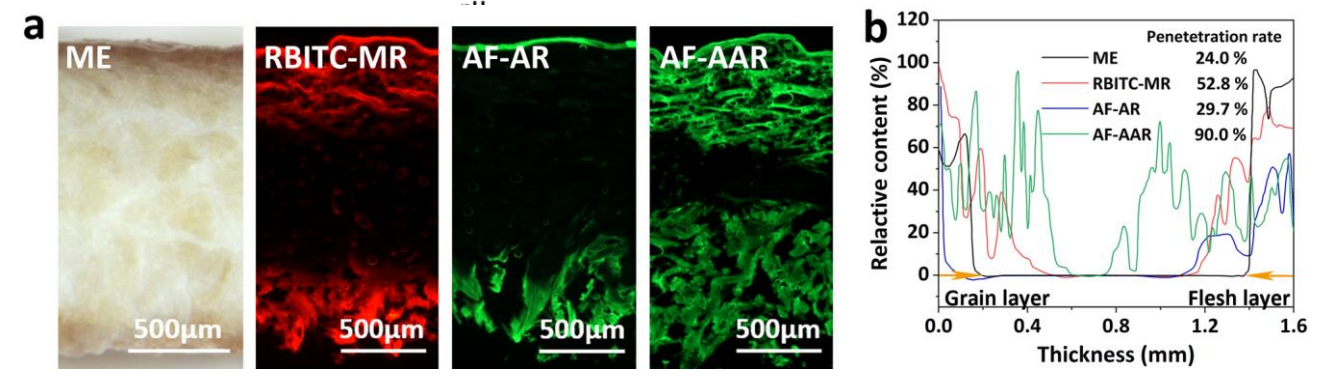
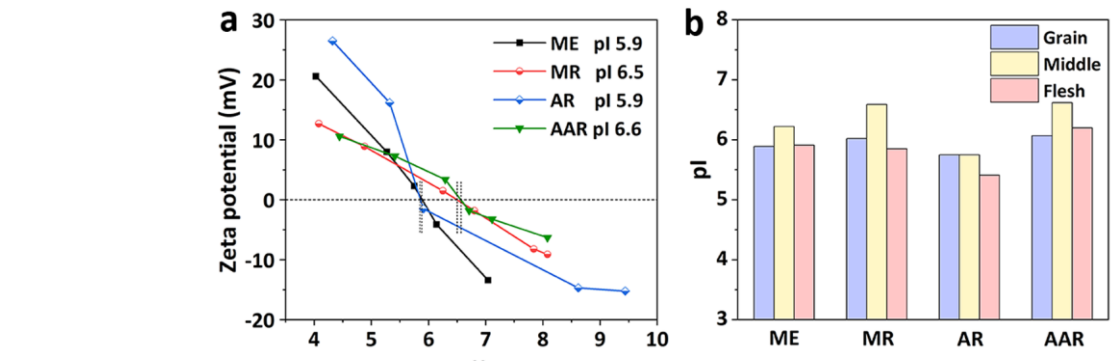
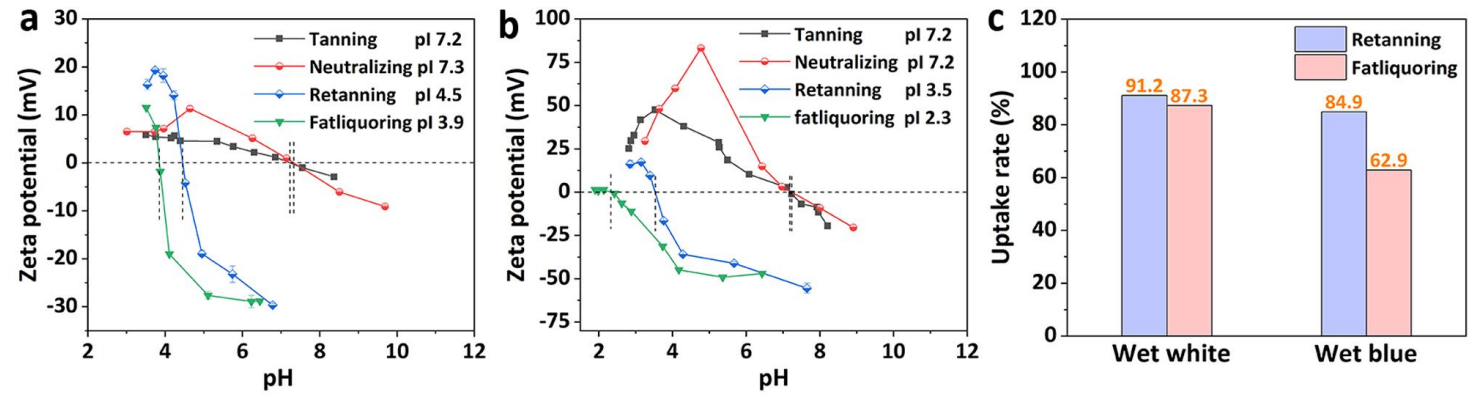
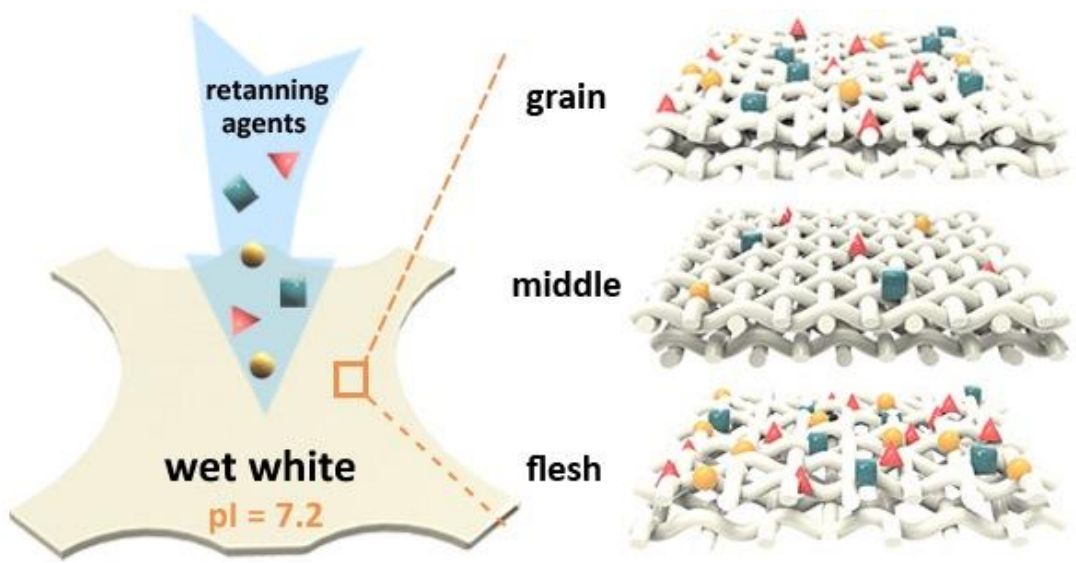


GLU: pI 4.7

5. Design of Cr-free tanning agent: Charge

Charge regulation of tanned leather

Interaction between retanning agents and wet white



Conclusions

- ◆ Cr-free tanning agent can be prepared by **biomass** to give leather sustainability and biodegradability.
- ◆ The strategy of **multiscale mass transfer and crosslinking** of tanning agent can guide the design of Cr-free tanning agent.
- ◆ **Charge regulation** of tanning agent and leather plays an essential role in the construction of Cr-free tanning system.



Acknowledgements

- ◆ **National Natural Science Foundation of China (22278280)**
National Key R&D Program (2017YFB0308500)
- ◆ **Research team: Dr. Shi Bi, Dr. Zhou Jianfei, Dr. Yu Yue, et al**
- ◆ **Organizing Committee of the Conference**



Thank you for your attention

Dr. Wang Ya-nan
wangyanan@scu.edu.cn

