Oxidation of Lignin Using H_2O_2–O_3

Synergistic System for sustainable leather manufacturing

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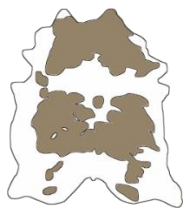
Main contents

- Background
- Tanning application
- Retanning application

Background

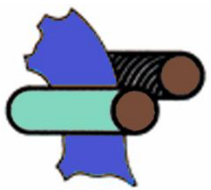
- **Tanning is the key process—Post-tanning is the "golden touch"**



Raw hides

Beamhouse →

Tanning →



Shaving →

Post-tanning →

Crust leather

Chrome ore

Non-renewable

»»

Chrome tanning agent

Sustainability?

Aromatic syntan

«

Petrochemicals

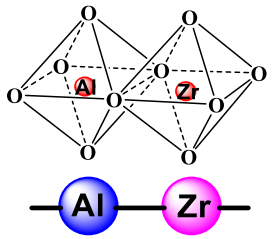
Non-renewable

Innovative renewable tanning and retanning agents are expected to enhance leather sustainability

Background

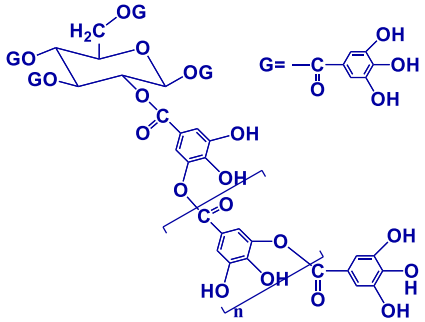
Chrome-Free tanning agent

Tanning agents

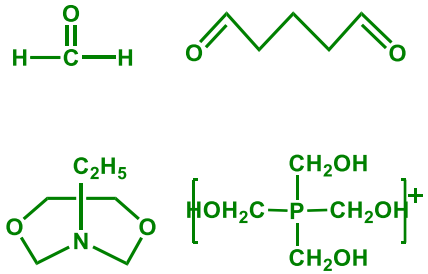


Al–Zr tanning agent

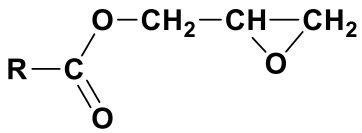
Similar cationic nature to Cr



Vegetable tannin

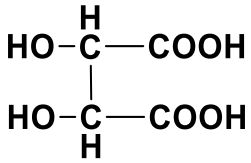


Aldehyde tanning agent

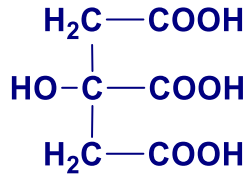


Epoxy tanning agent

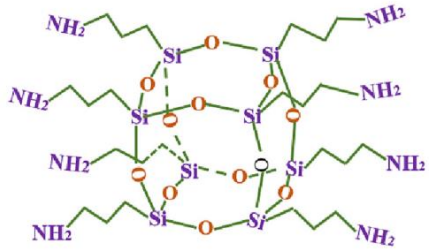
Ligands for Al–Zr



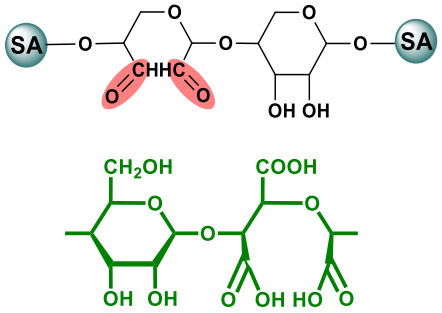
Tartaric acid



Citric acid



Silsesquioxane



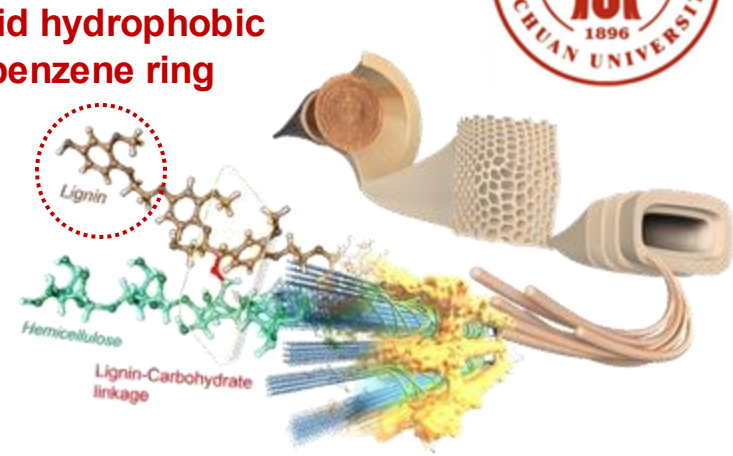
Oxidized polysaccharides

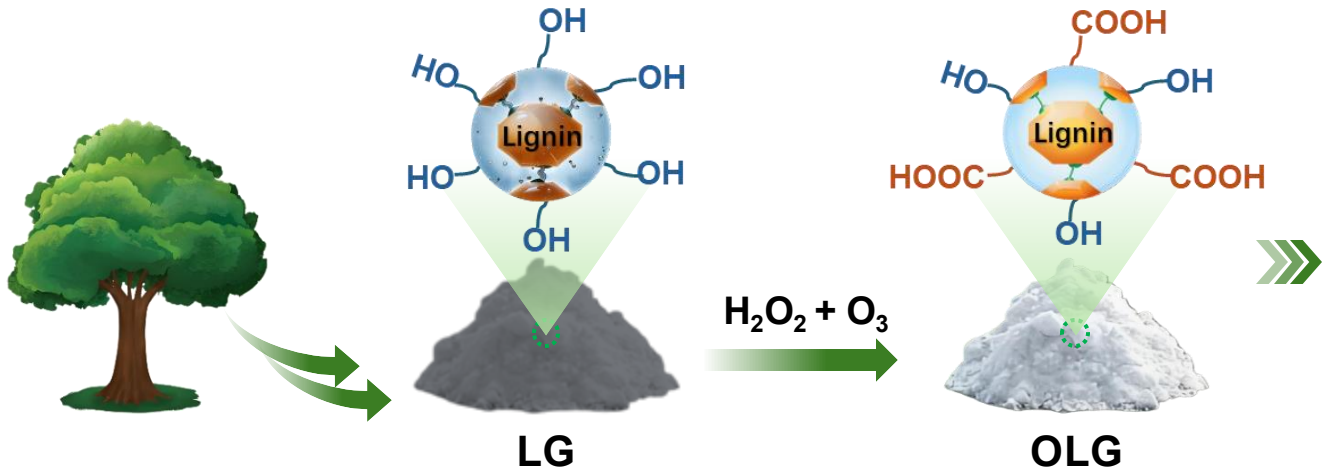
Defects: derived from petrochemicals; insufficient rigidity and hydrophobicity

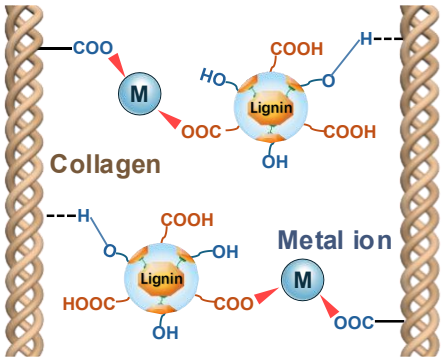
Background

Lignin-based leather chemicals

- Multi-functional groups, abundant modification sites
- The only renewable resource that provides aromatic compounds





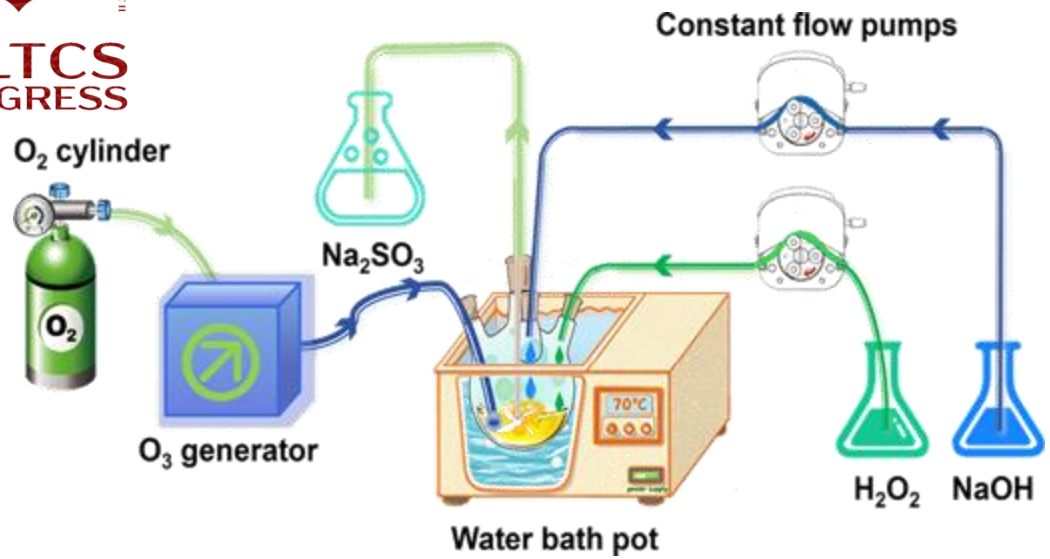


- Light color
- Strong tanning/filling effect
- Green sustainability

Rich reactivity groups + Controllable molecular weight + Light color → Tanning agent / Retanning agent

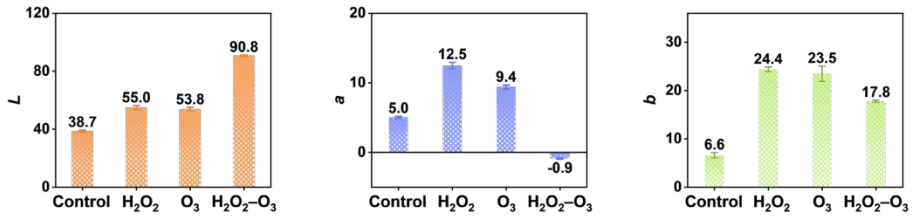
Tanning application

Colority of OLGs

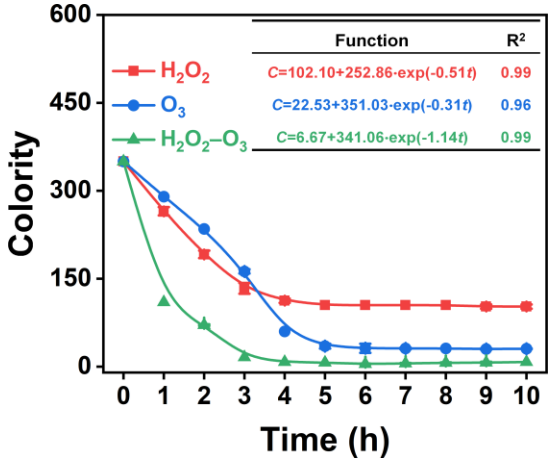


Reaction equipment

Color parameters

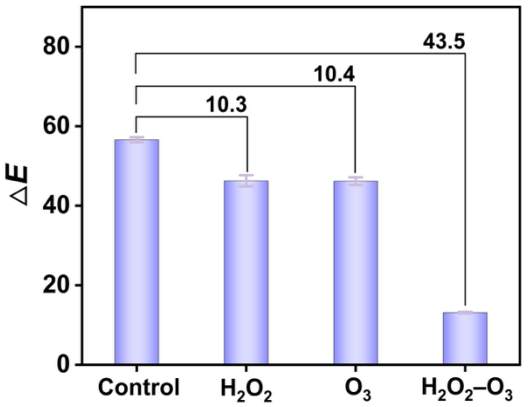


Colority

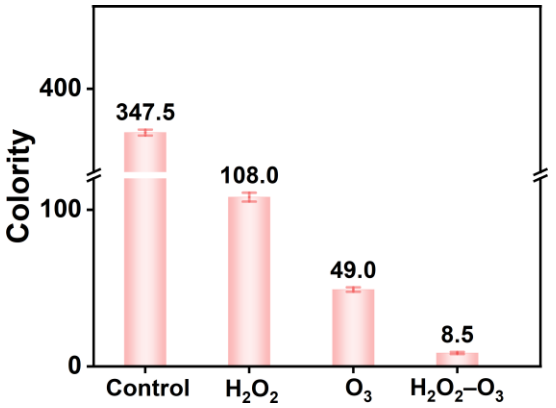


Appearance

Solid color



Liquid colority

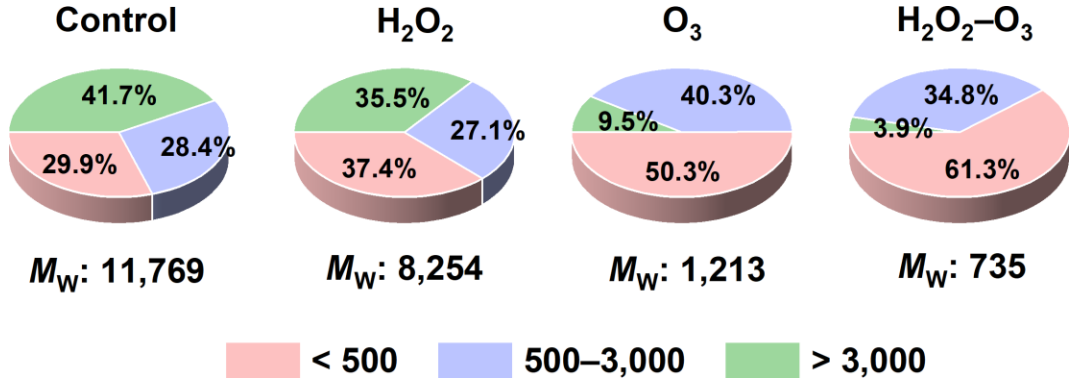


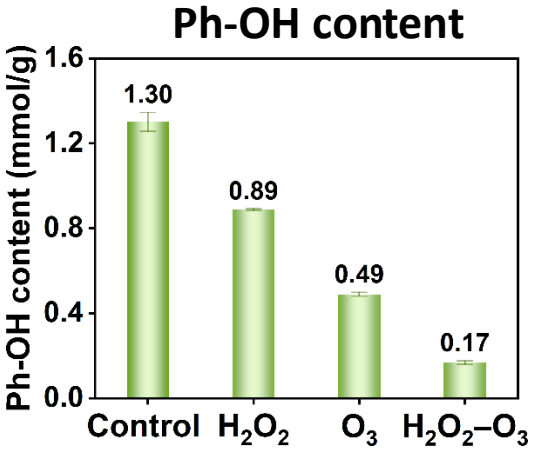
H_2O_2–O_3 system shows a synergistic effect on lignin decolorization

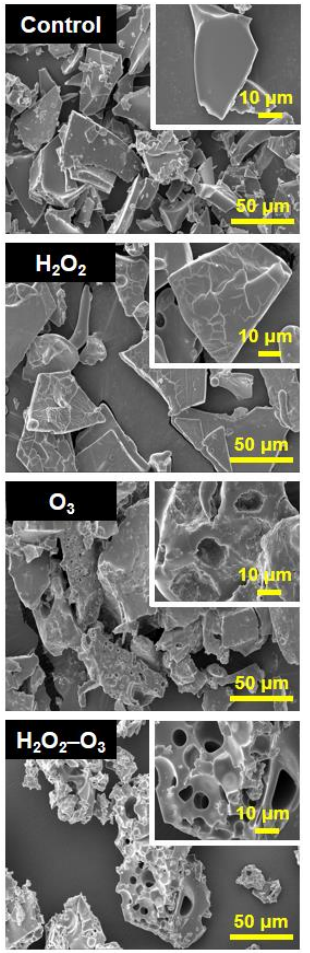
Tanning application

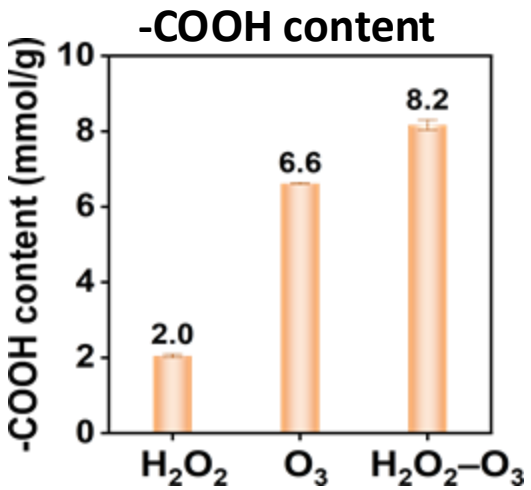
Chemical structure of OLGs

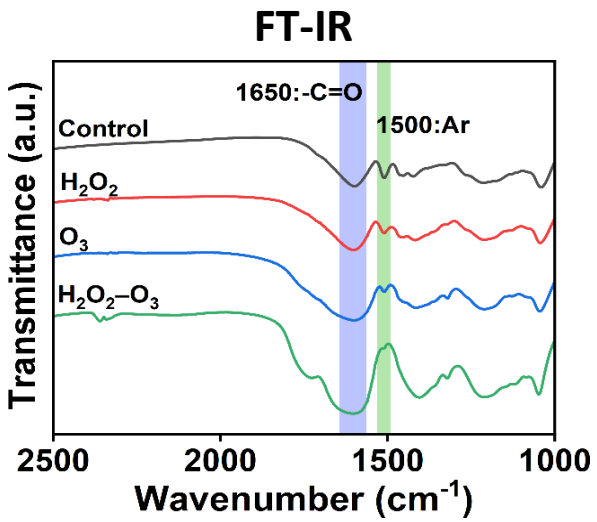
Molecular weight

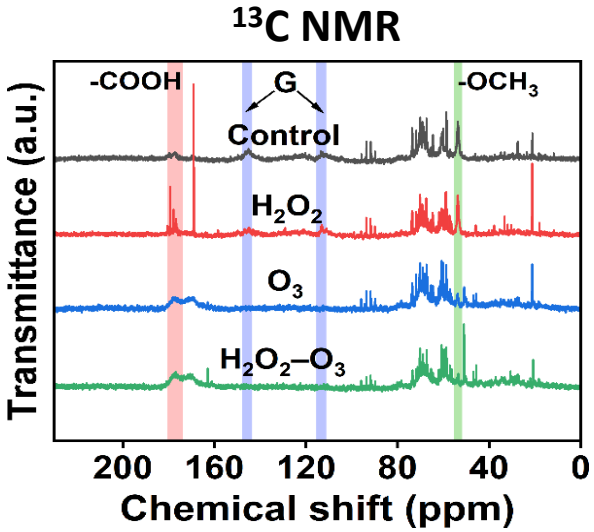










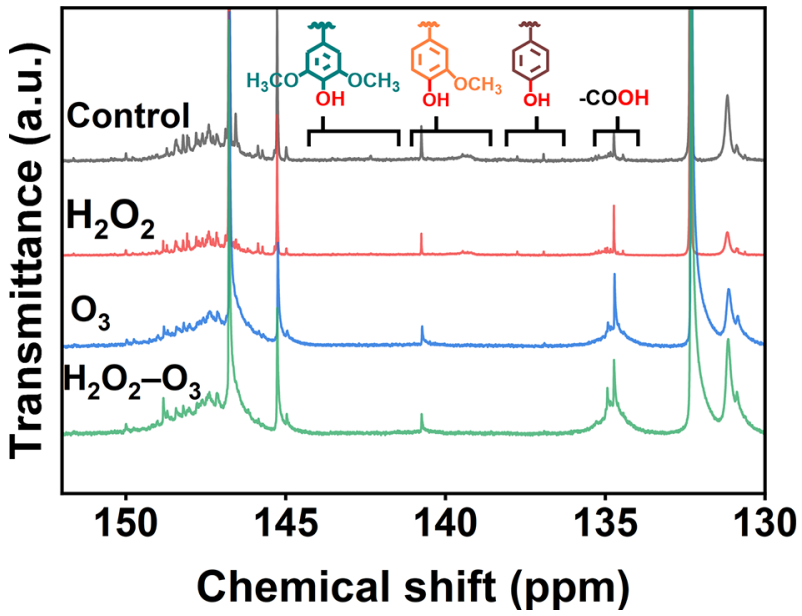


H_2O_2–O_3 system increased the -COOH and decreased the *M*w of the OLGs

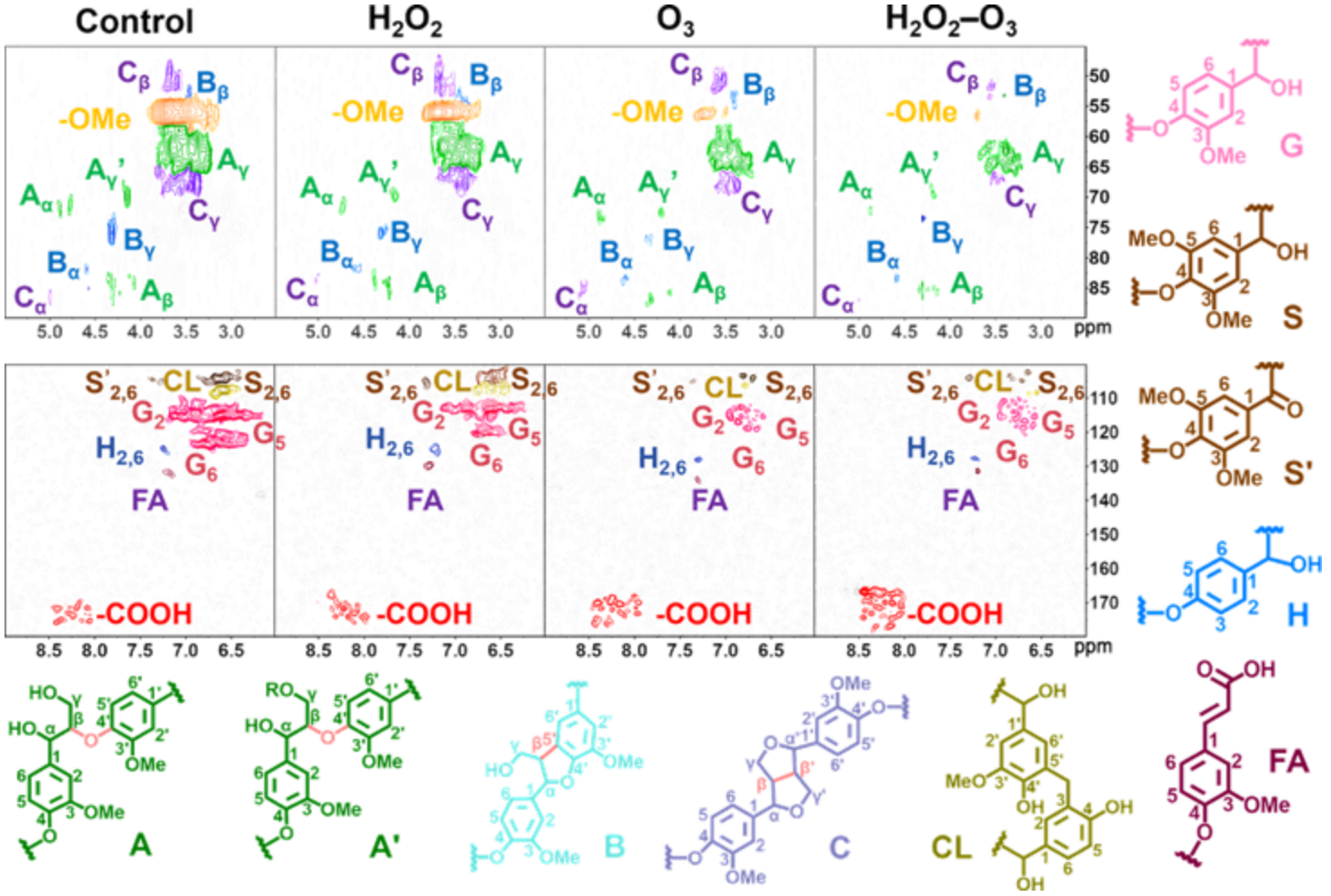
Tanning application

Chemical structure of OLGs

^{31}P NMR



2D HSQC NMR



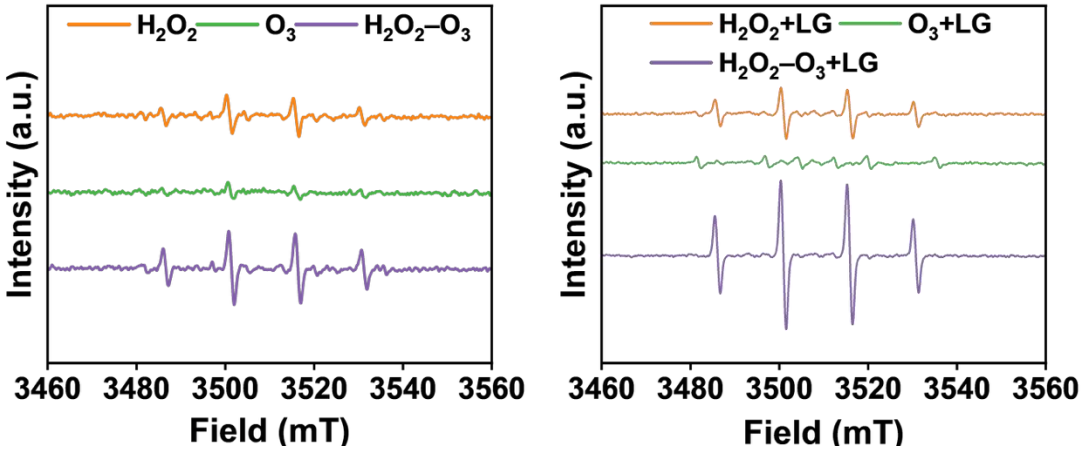
- Ring open
- C-C cleavage
- -OH oxidation
- C-O cleavage

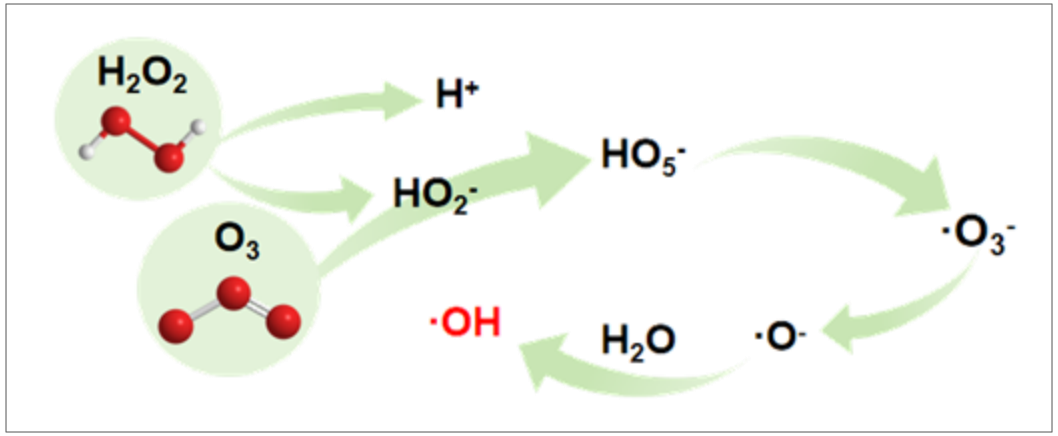
H_2O_2–O_3 system oxidizes both side-chain and aromatic ring structures

Tanning application

Role of radicals in oxidation

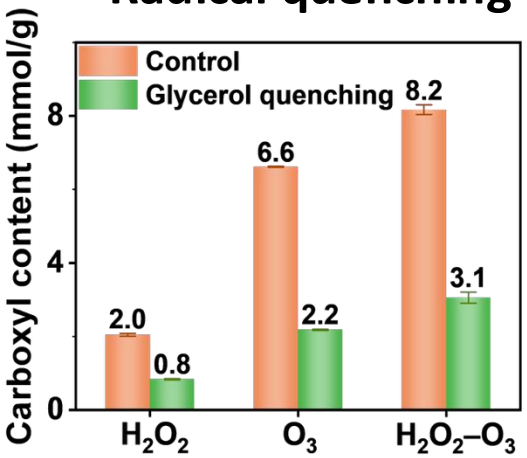
EPR

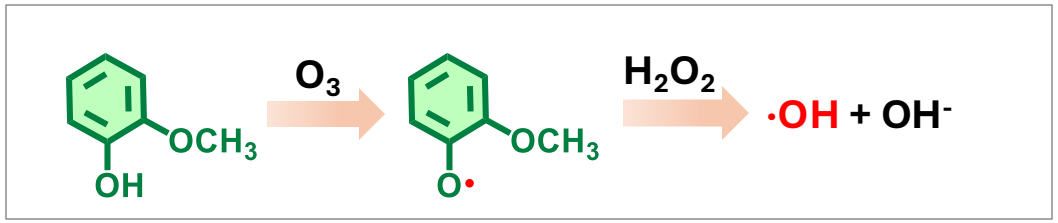


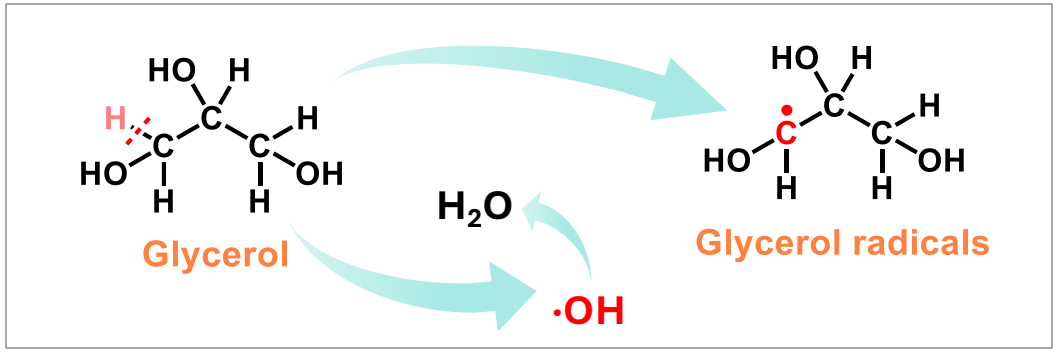


- ·OH: key reactive species
- H_2O_2–O_3 facilitates efficient ·OH generation
- Enhancing decolorization and functional groups

Radical quenching



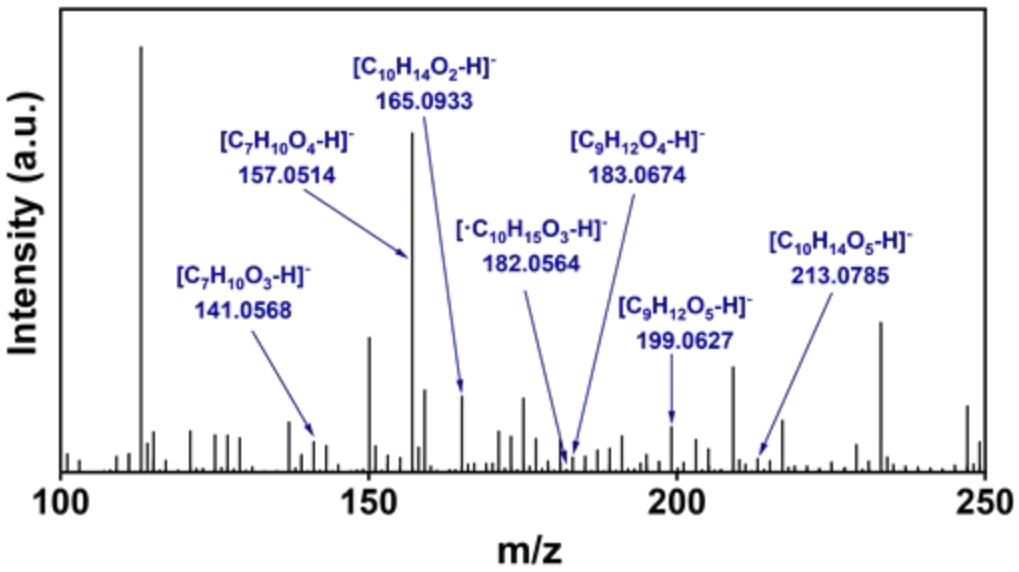




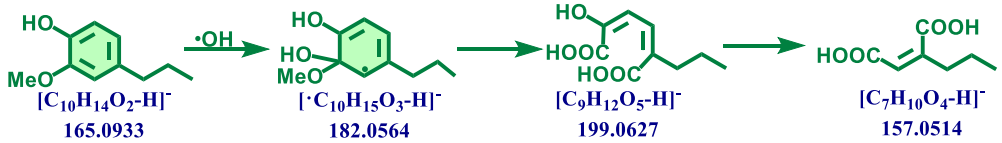
Tanning application

Analysis of oxidized lignin model compound

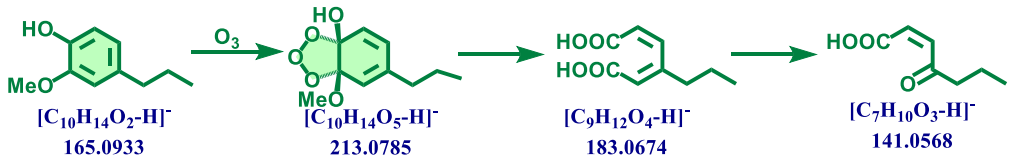
ESI-MS



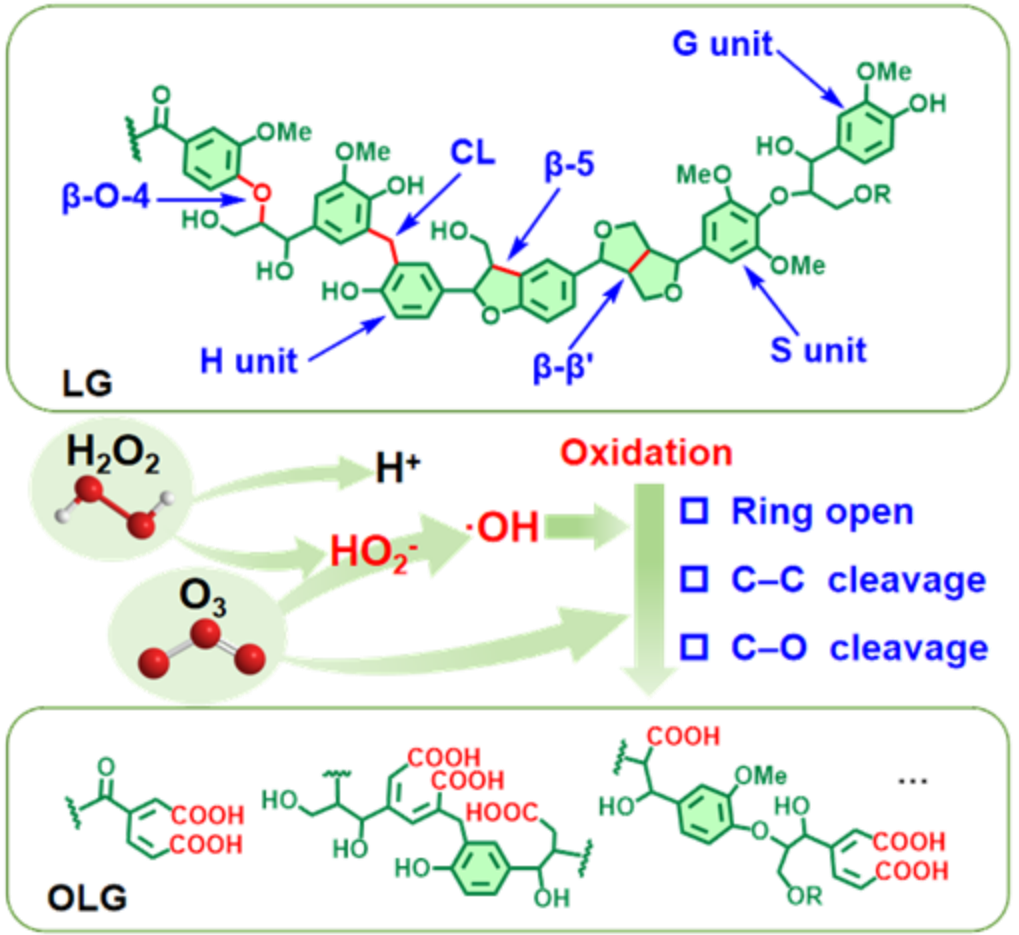
Path 1



Path 2



Oxidation mechanism

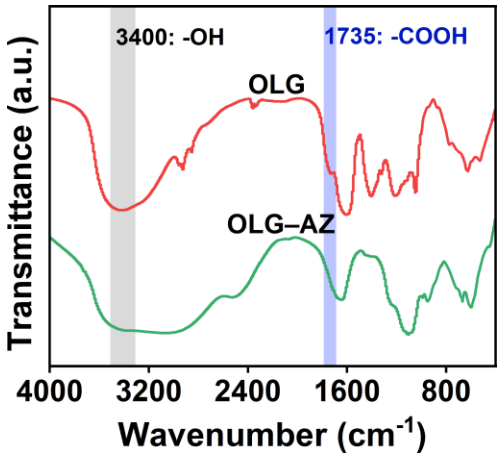


·OH and O_3 react with LG, facilitating benzene ring opening and –COOH formation

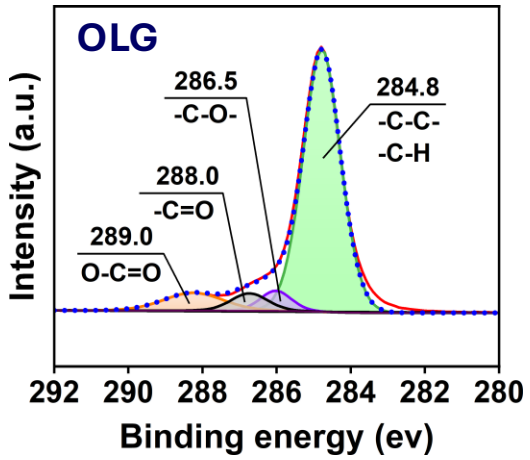
Tanning application

Tanning mechanism of OLG–AZ

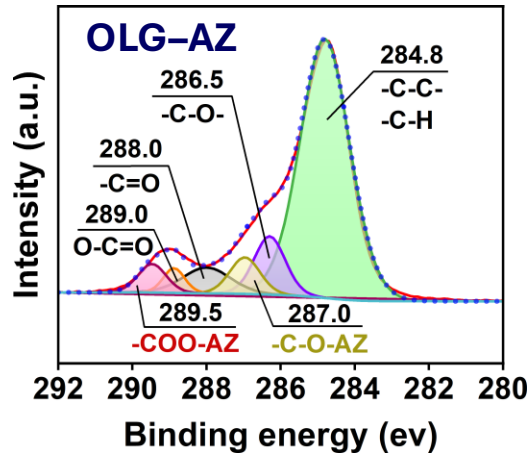
FT-IR



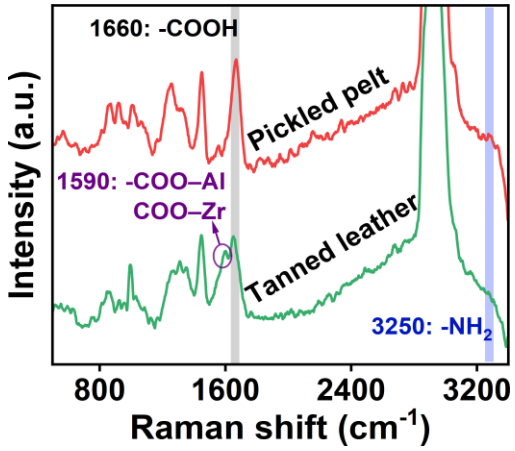
XPS



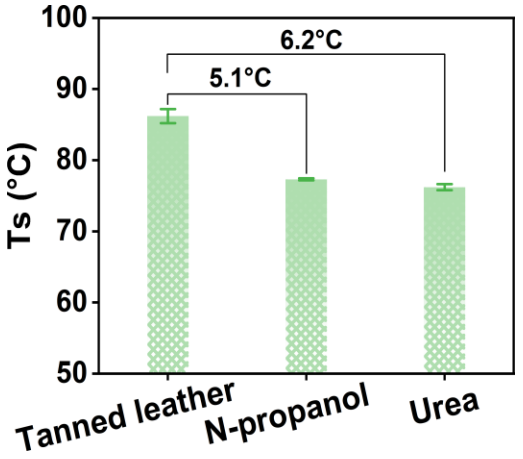
XPS

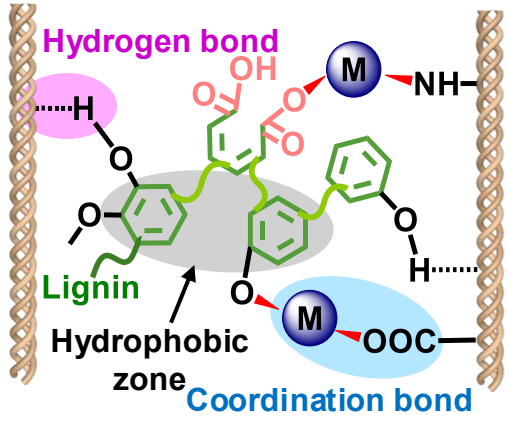


Raman



Washing

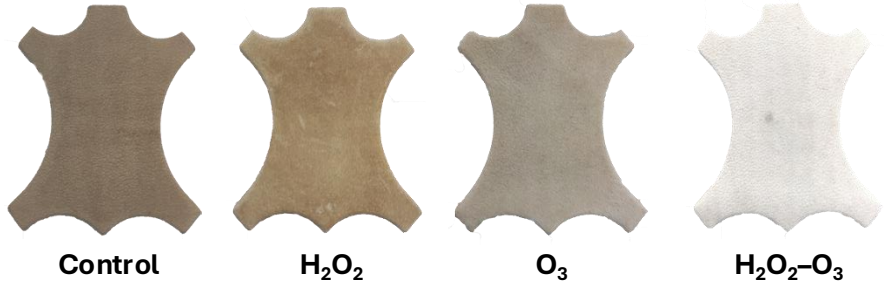


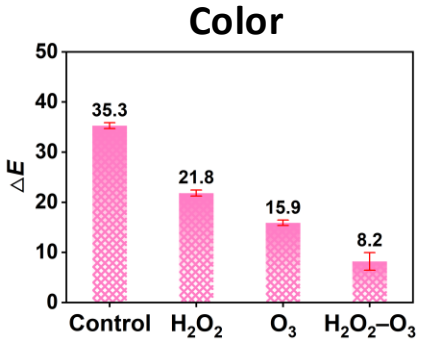


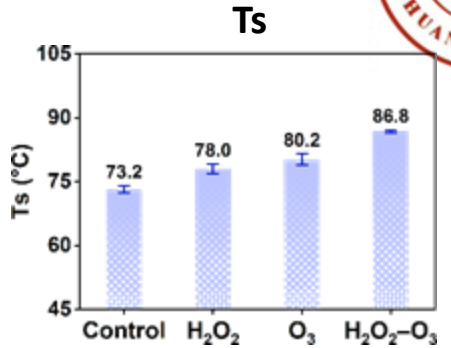
Cross-linking network formed by coordination bonds, hydrogen bonds, and hydrophobic interactions

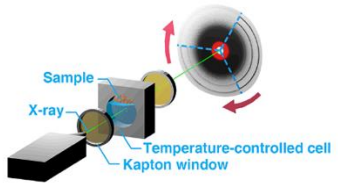
Tanning application

Tanning effects of OLG–AZ

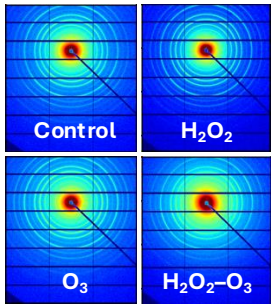


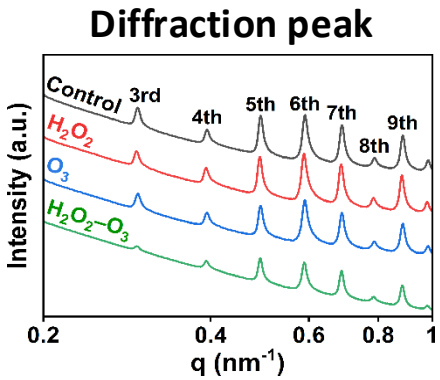


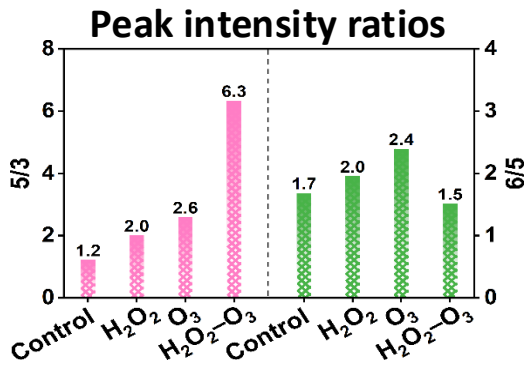


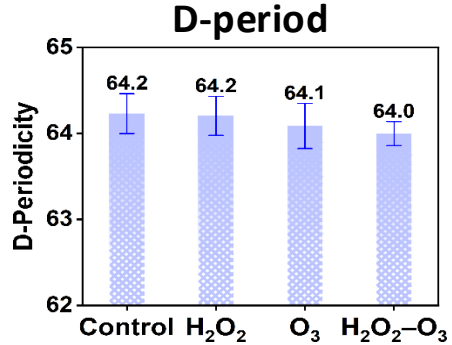


SAXS

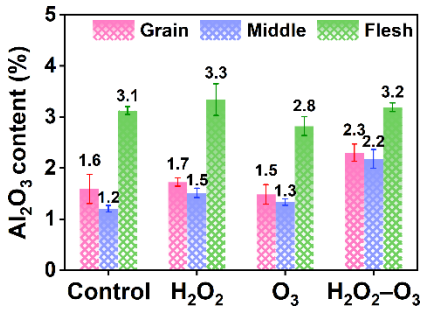


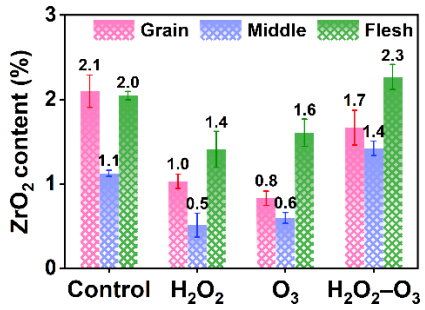


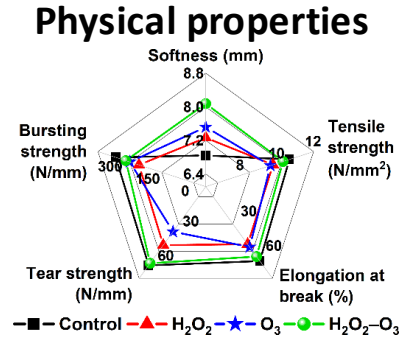


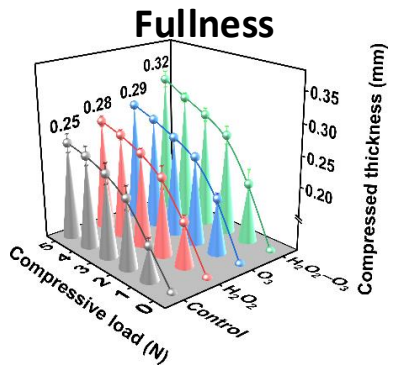


Metal distribution









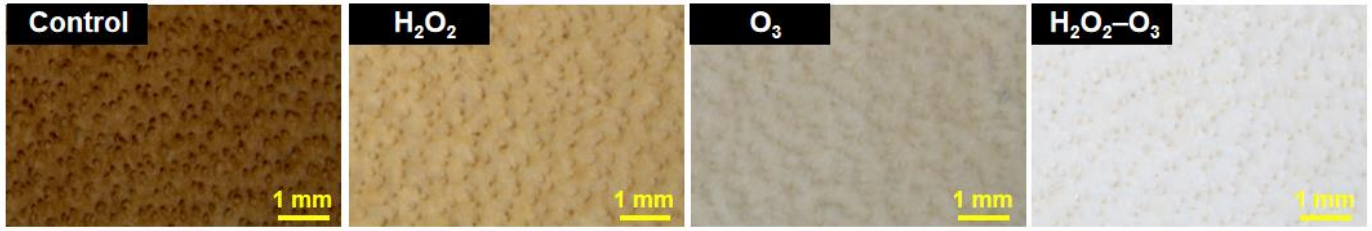
White color, high Ts, uniform AZ distribution, and desirable physical properties

Tanning application

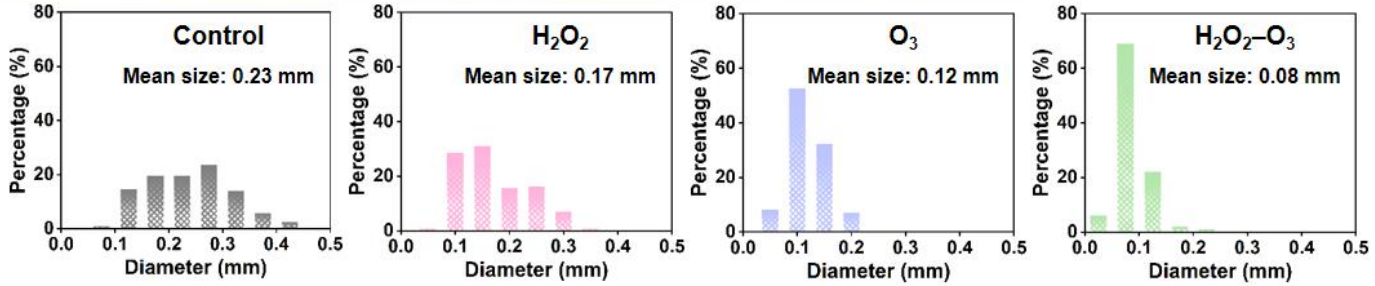
Morphology analysis

LG: dark brown; OLG: light color

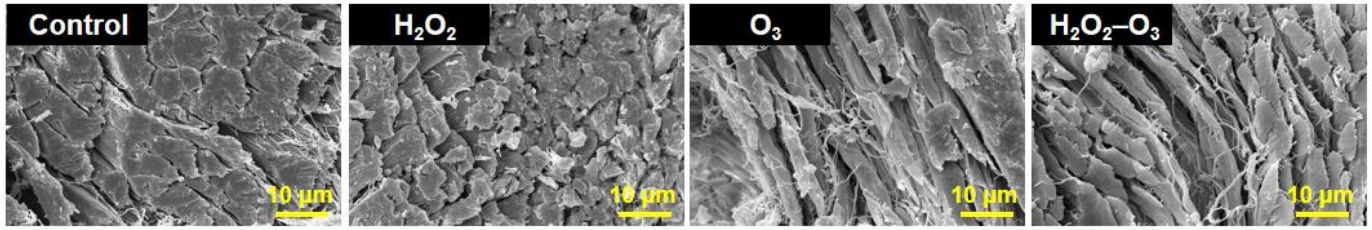
Grain surface



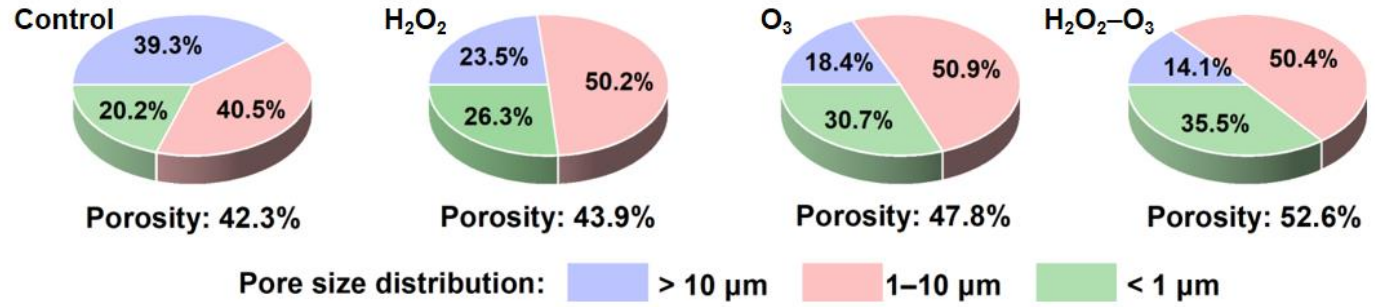
Pore size distribution



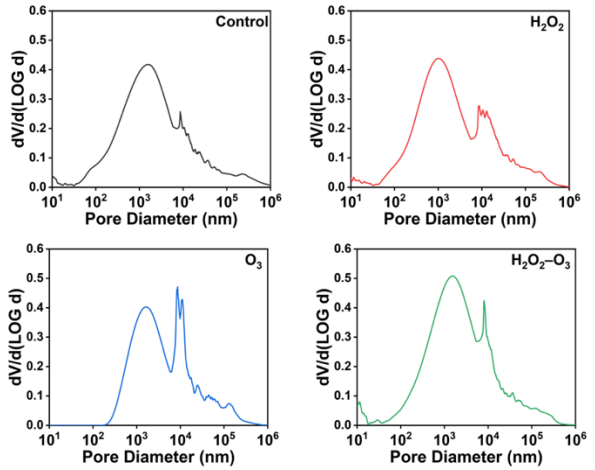
SEM Images



Porosity and distribution



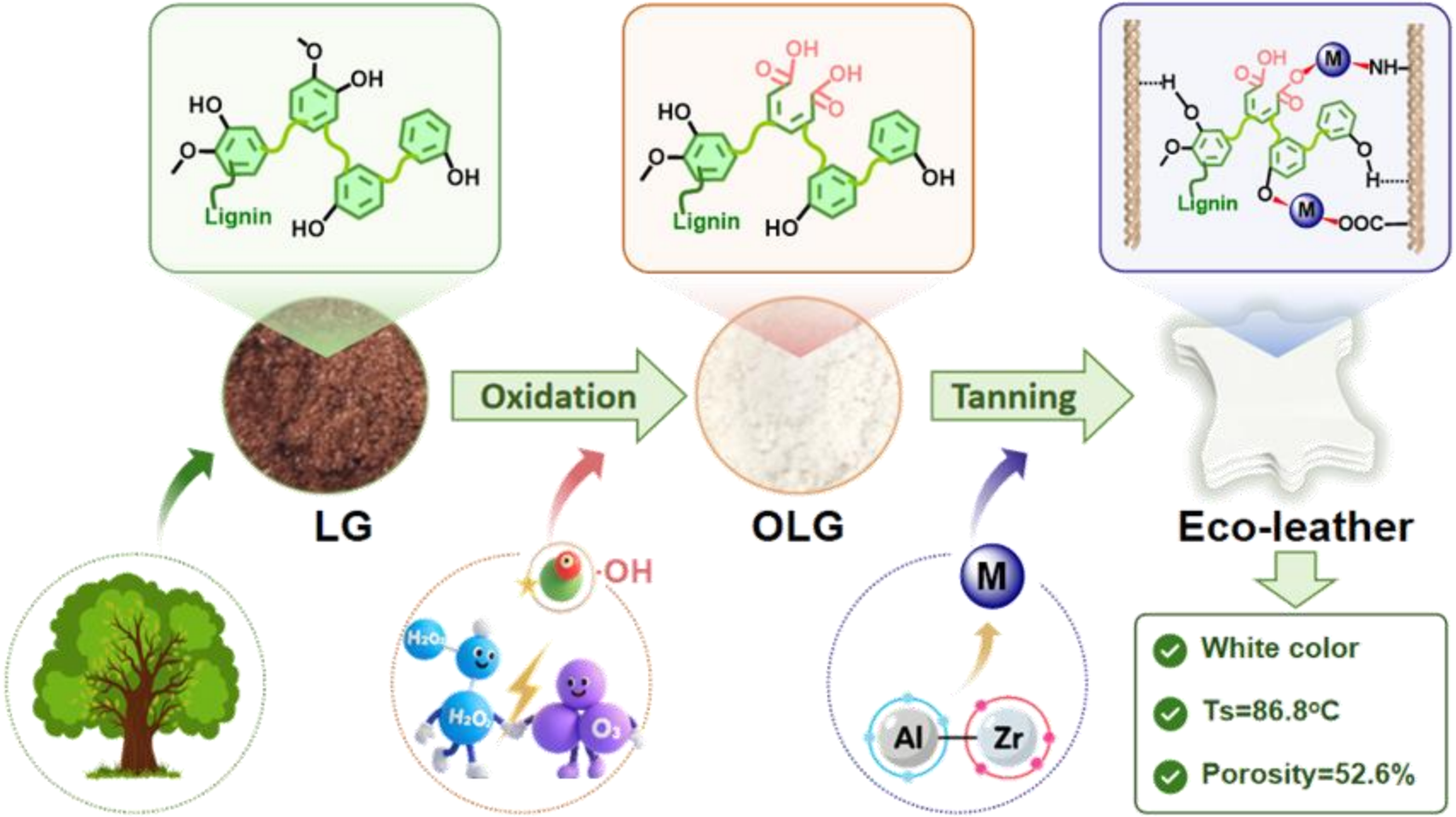
Porosity distribution



- Fine grain, 0.08 mm pore size
- High fiber dispersion: 52.6%
- Demonstrate its practicality

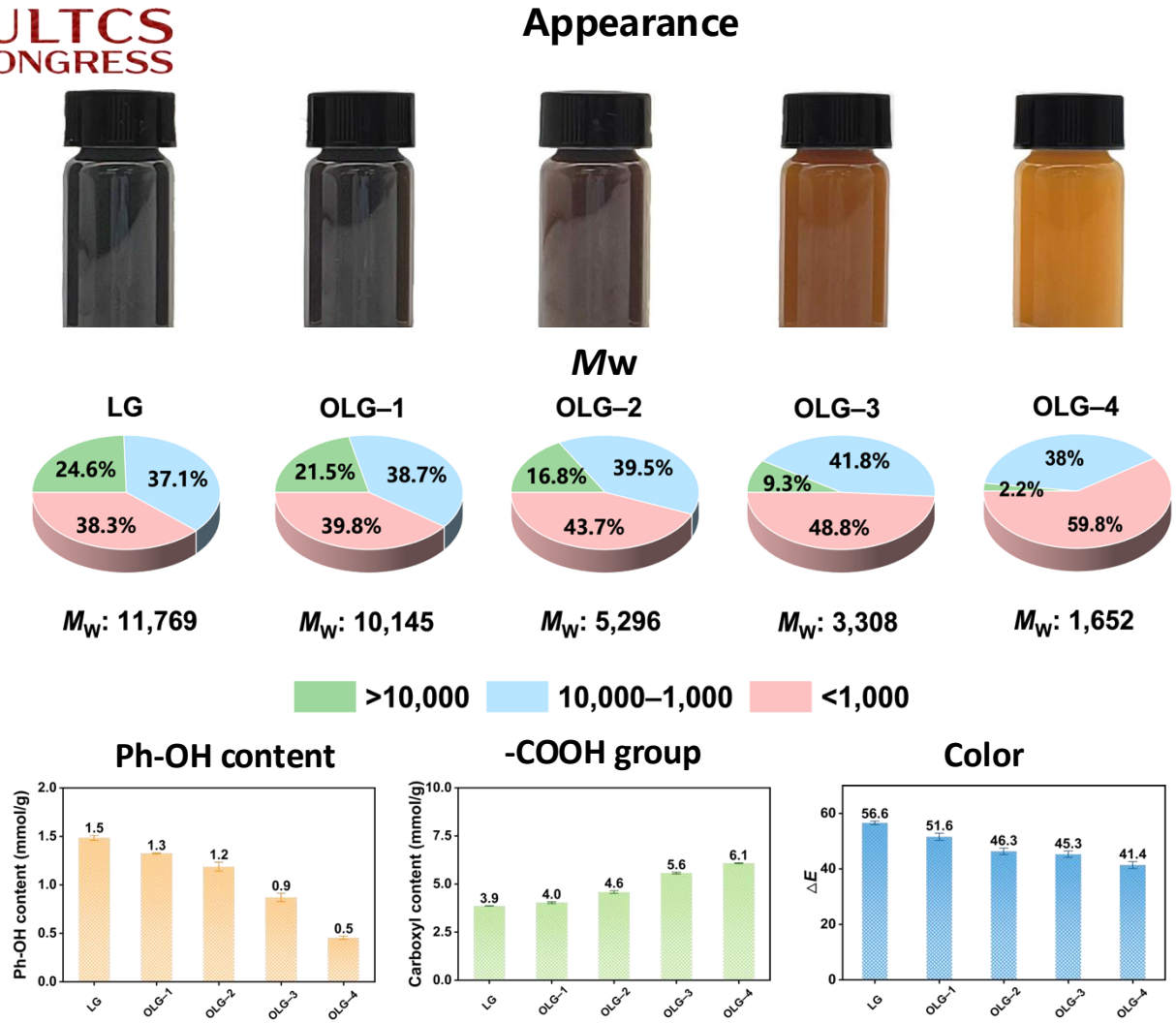
Tanning application

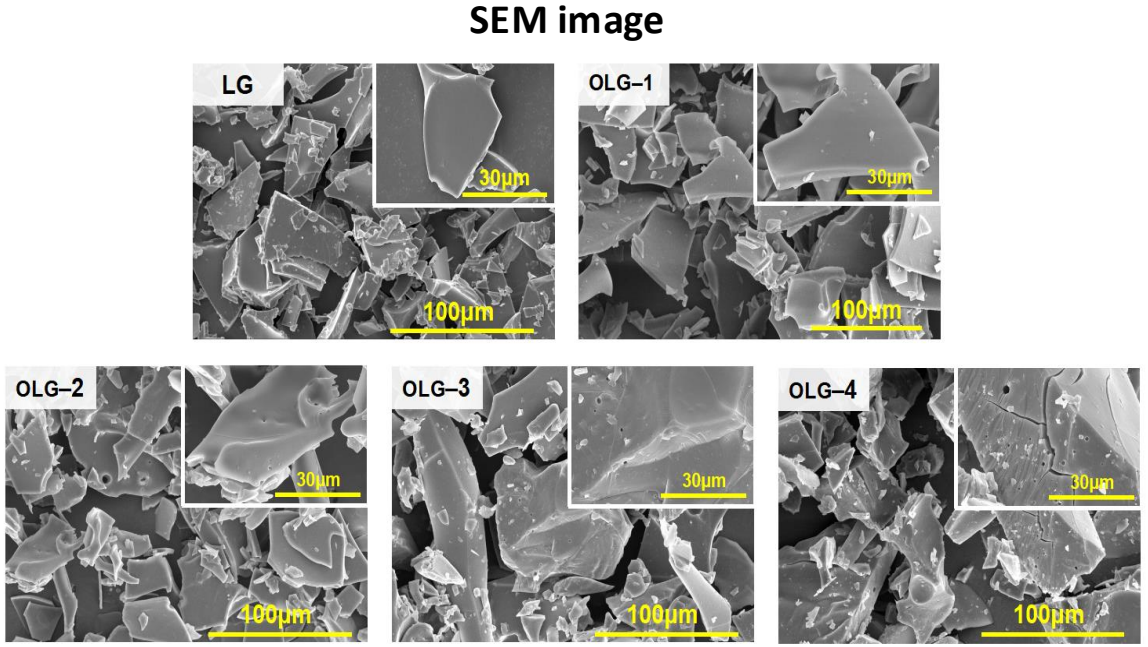
- **Summary**



Retanning application

Chemical structure of retanning agents



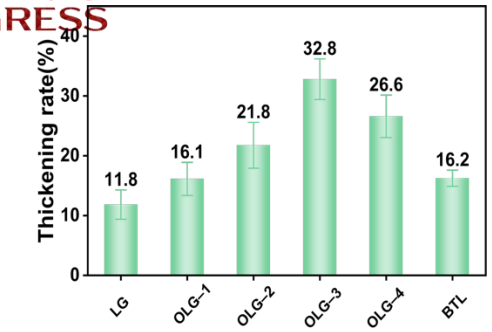


- Controllable color, molecular size, and functional group content
- Different chemical structures work better for different post-tanning needs

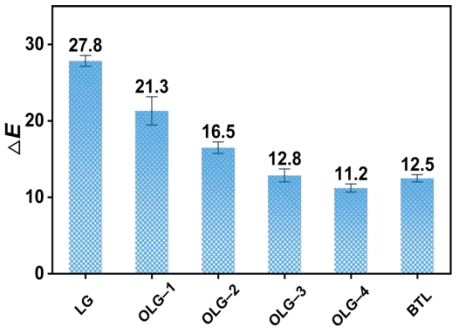
Retanning application

Retanning effects of OLGs

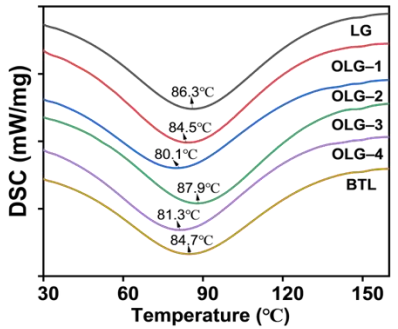
Thickening rates



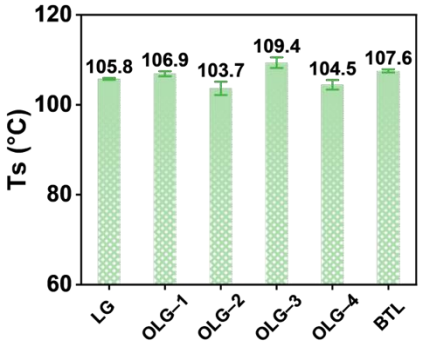
Color



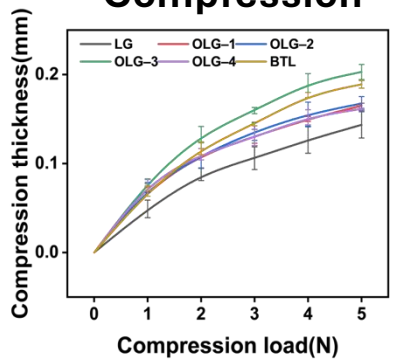
DSC



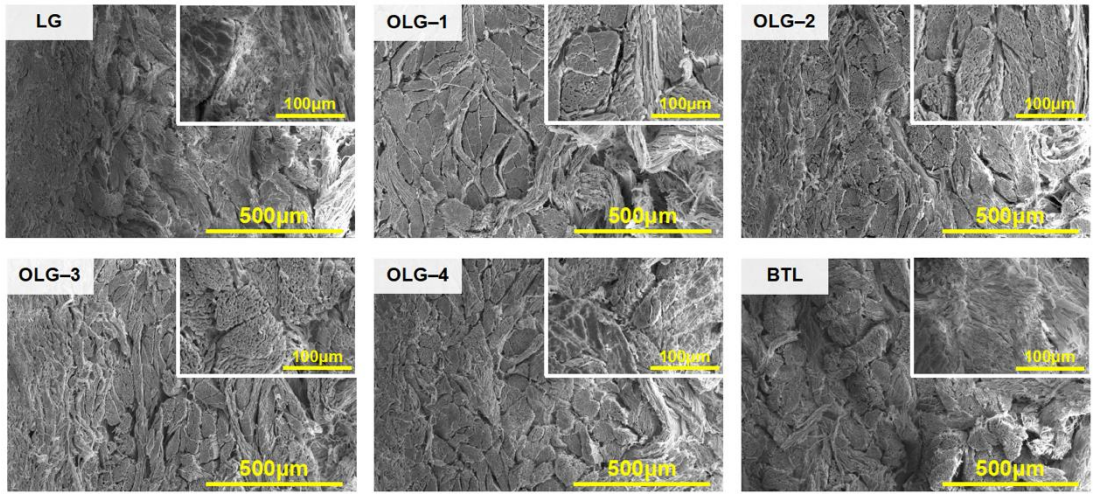
Ts



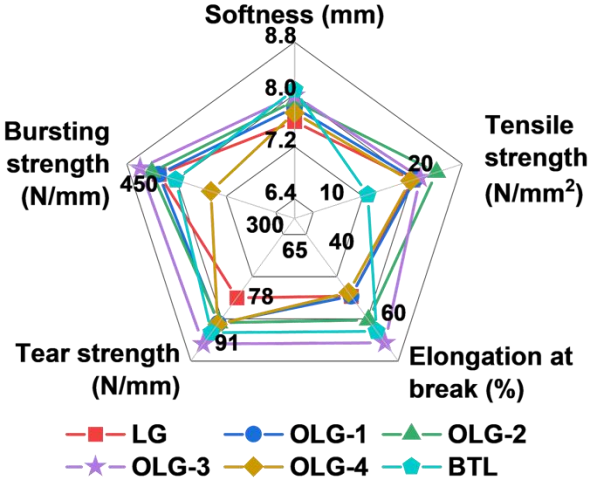
Compression



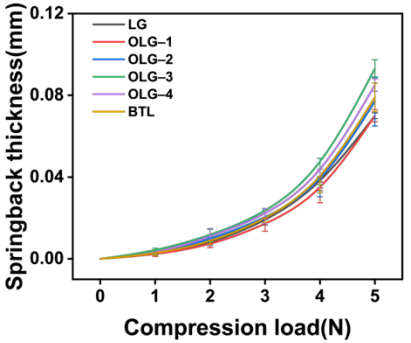
SEM images



Physical properties



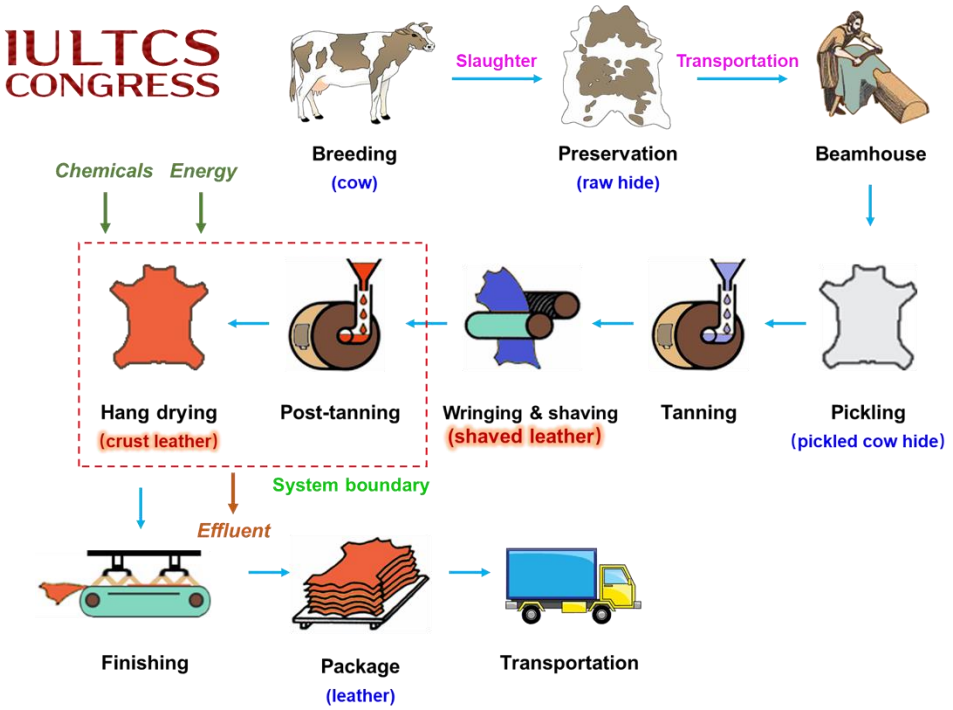
Resilience



OLGs-3 provides desirable retanning effects compared to traditional aromatic syntans

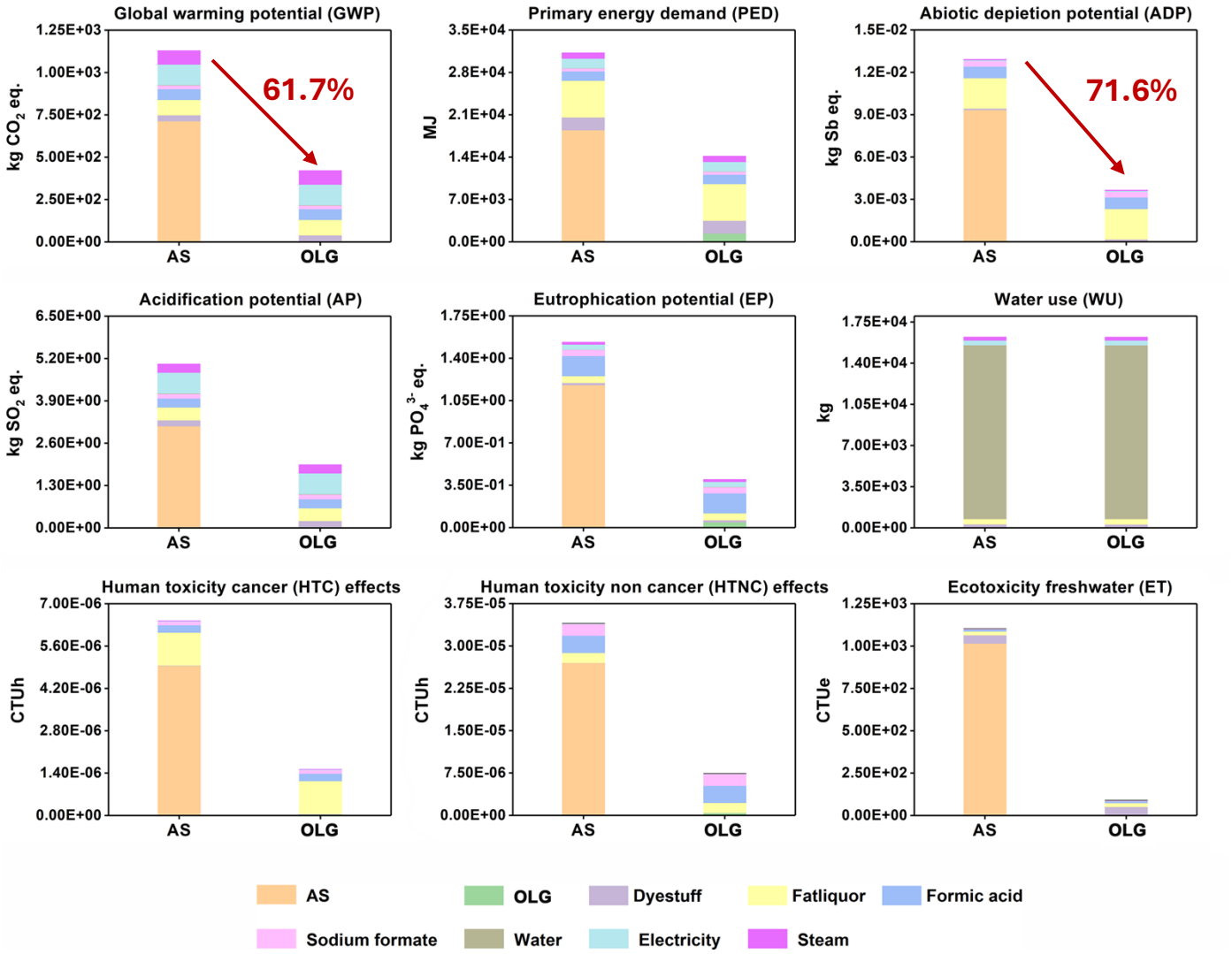
Retanning application

Life cycle assessment



- **61.7%** reduction in carbon emissions
- **71.6%** reduction in resource consumption
- Low ecotoxicity and human toxicity

AS (aromatic syntan) *vs.* OLG



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- **Other co-authors:**

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  Prof. Ya-nan Wang

  Prof. Bi Shi

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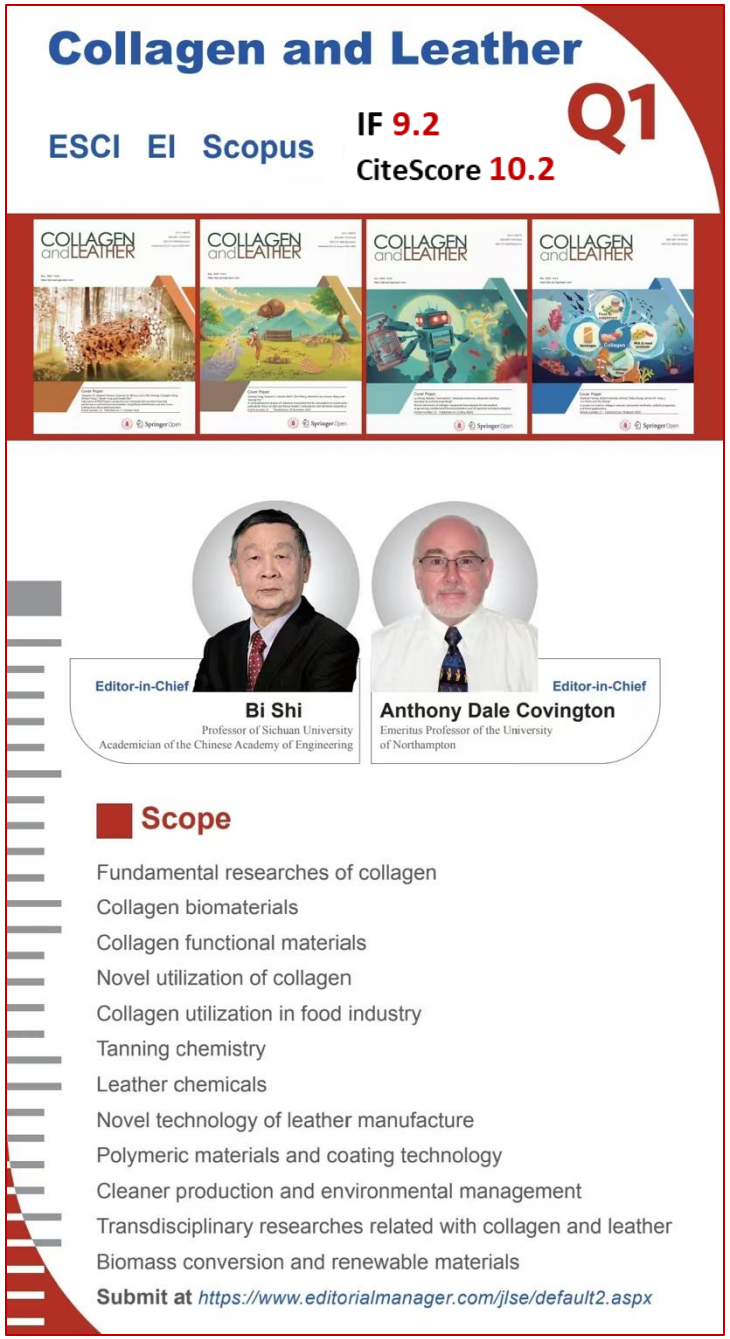

COLLAGEN and LEATHER

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Scope

Fundamental researches of collagen
Novel utilization of collagen
Tanning chemistry
Leather chemicals
Novel technology of leather manufacture
Polymeric materials and coating technology
Cleaner production and environmental management
Collagen biomaterials
Collagen functional materials
Collagen utilization in food industry
Transdisciplinary researches related with collagen and leather
Biomass conversion and renewable materials

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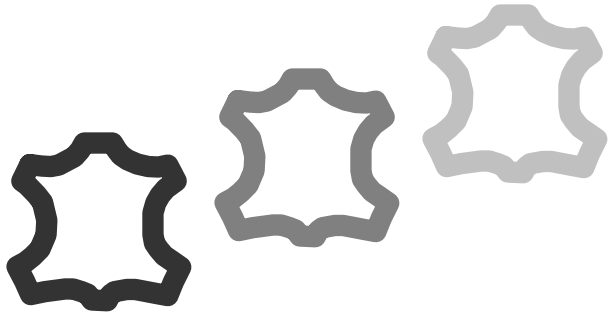
Thank you for your attention!



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