

# All-wood-based antimicrobial hydrogel fabricated by digital light processing (DLP) printing

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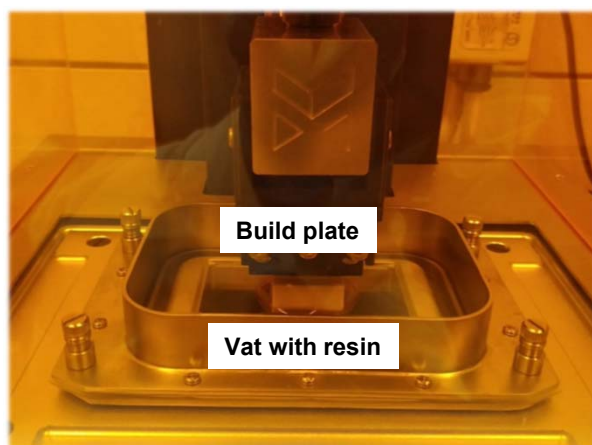
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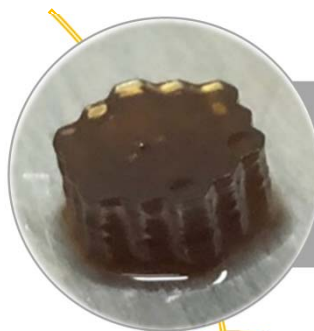


# Outline

(DLP printer)

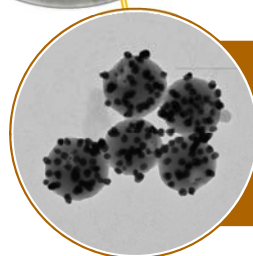


- Stable customized imaging
- Excellent spatial resolution
- Rapid fabrication speed

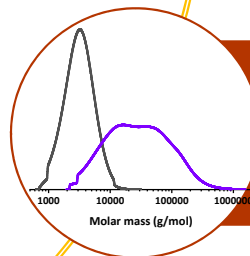


DLP printing

Photo-crosslinkable polysaccharide-based resin



Lignin nanosphere supported Ag nanoparticle (LNP@Ag)



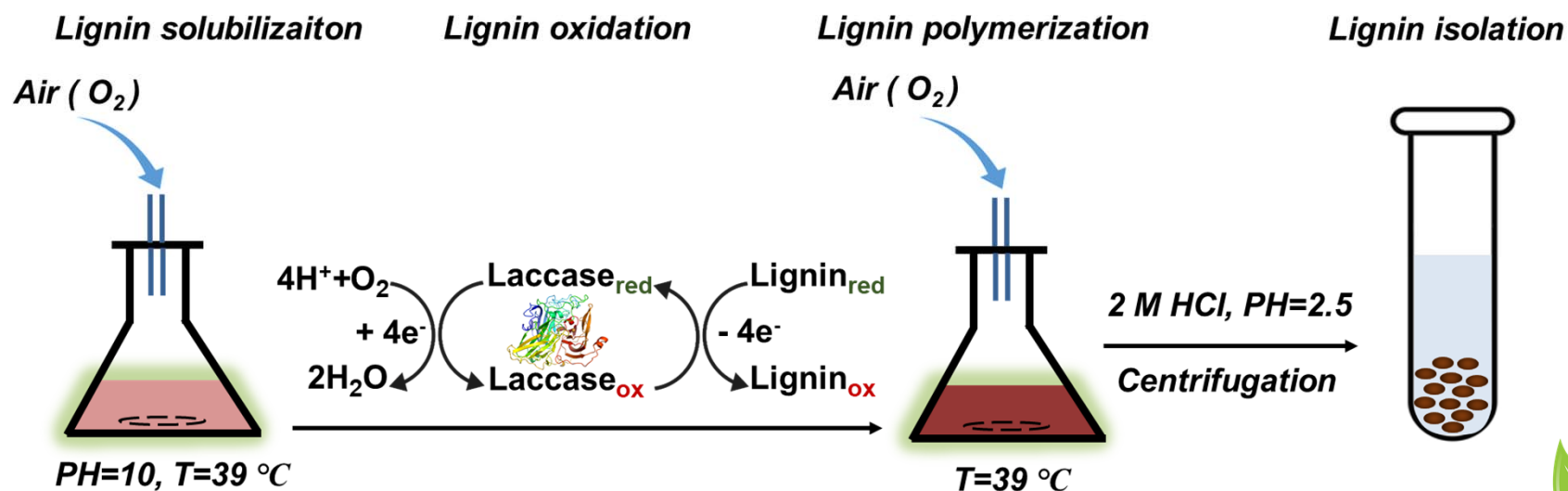
Laccase-induced lignin polymerization  
(Lignin-structure-property-performance)

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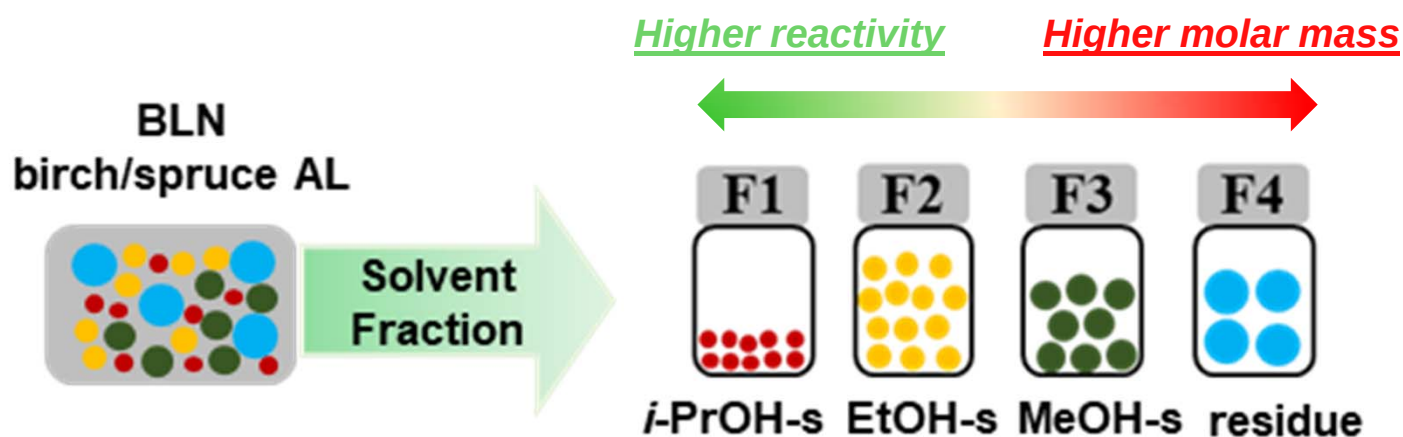
# Laccase-induced lignin polymerization

- fabrication of LNP@Ag demands LNP of sufficient alkali resistance in  $[\text{Ag}(\text{NH}_3)_2]^+$  (pH 11)
- hardwood (birch), softwood (spruce) alkaline lignins (AL), and lignin fractions



# Lignin sequential fractionation

- lignin fractions with narrow molar mass dispersity were obtained
- molar mass and condensation degree increased, while phenolic-OH decreased along the fractionation sequence



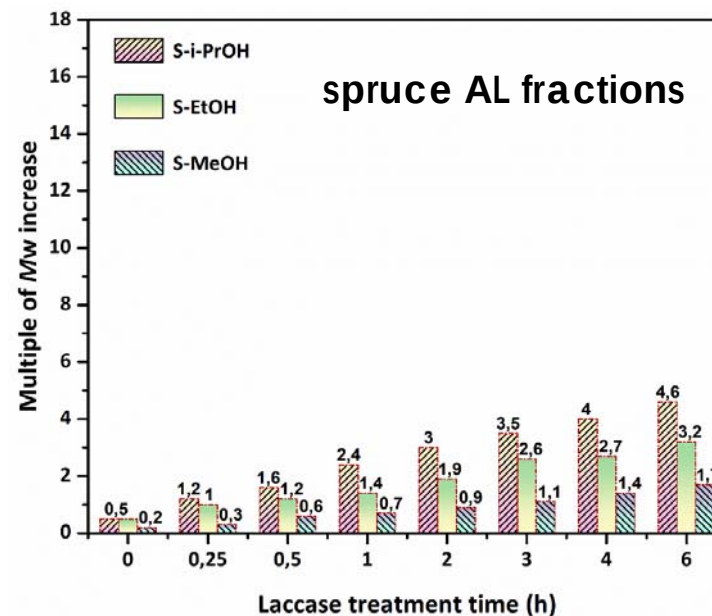
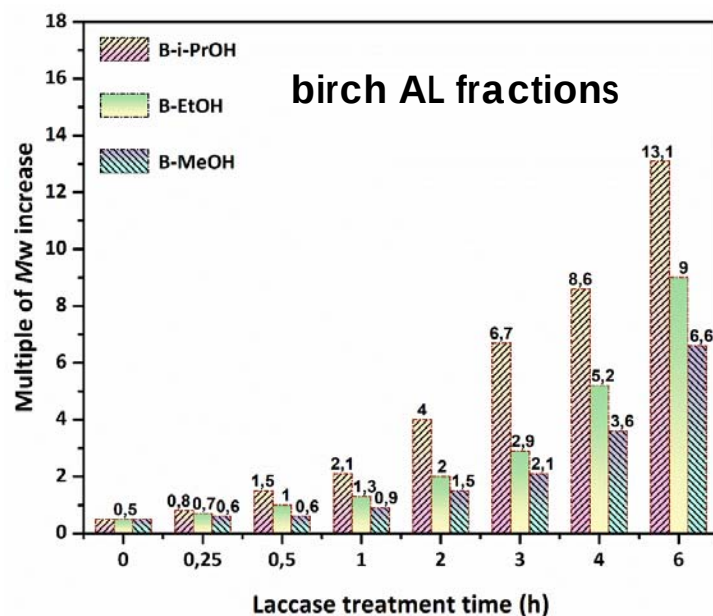
Wang L, Lagerquist L, Zhang Y, et al. Tailored Thermosetting Wood Adhesive Based on Well-Defined Hardwood Lignin Fractions. *ACS Sustainable Chemistry and Engineering*. 2020;8(35):13517-13526.

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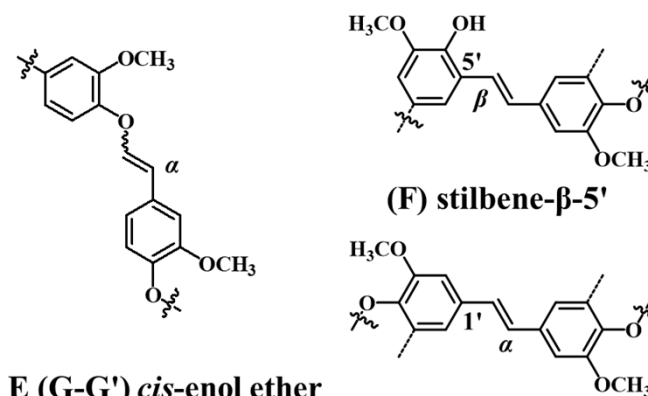
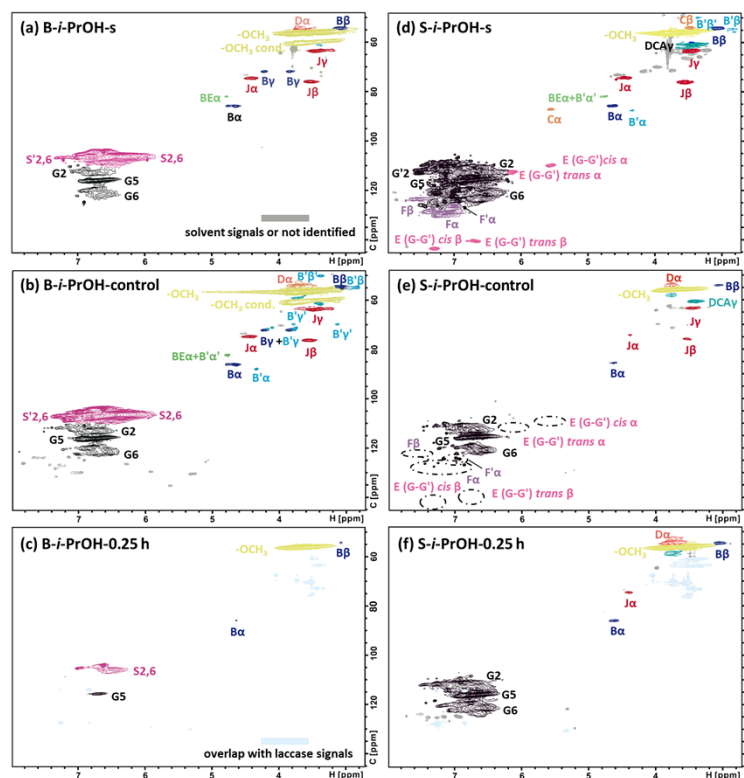


# Molar mass of laccase-treated lignin

- AL fractions with low  $M_w$  and condensation degree as well as high content of phenolic-OH groups, reached higher molar mass polymerization degree



# Structural changes of lignin (HSQC)



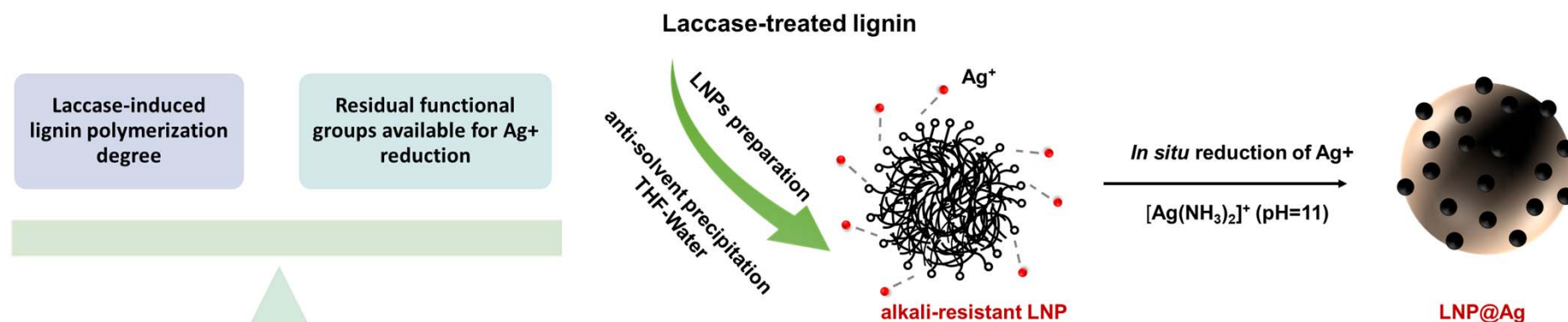
E (G-G') *cis*-enol ether

E' (G-G') *trans*-enol ether (F') stilbene-β-5'

- pronounced lignin polymerization at aromatic ring of birch AL fractions
- prominent air-induced oxidation of aryl-vinyl moieties in spruce AL fractions

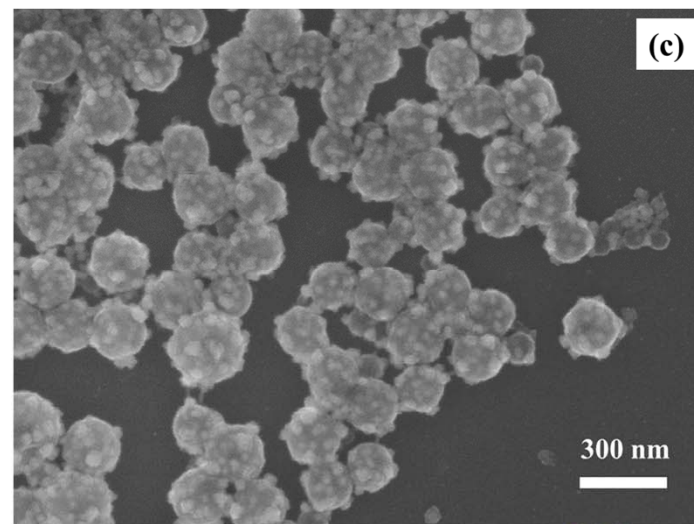
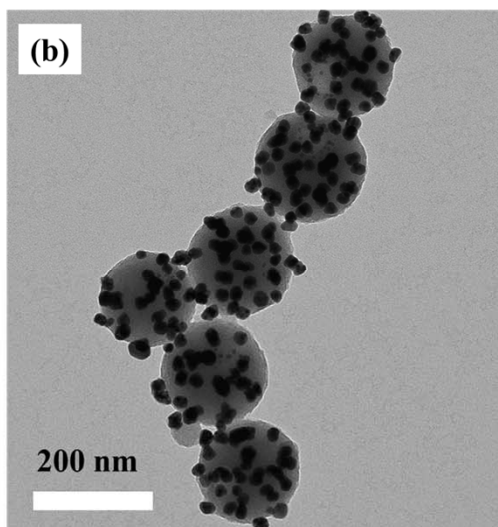
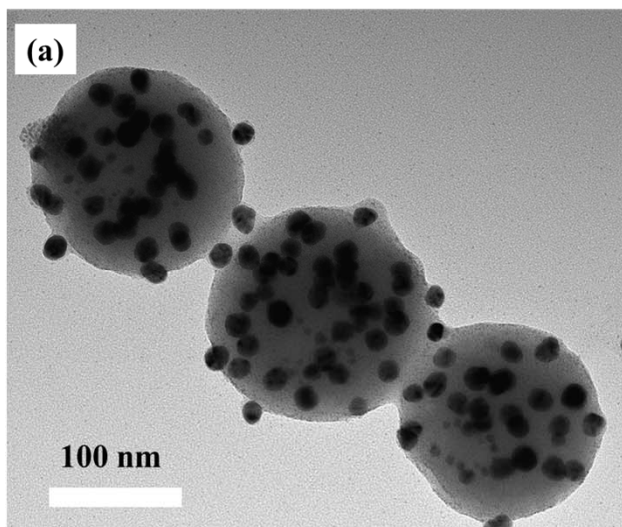
# Lignin nanosphere supported Ag nanoparticle

- laccase-polymerized lignin have the advantage of thermal stability and chemical tolerance (e.g., alkali)
- redox reaction between LNP (phenolic-OH and -OCH<sub>3</sub>) and Ag<sup>+</sup> precursor



# Morphology of LNP@Ag

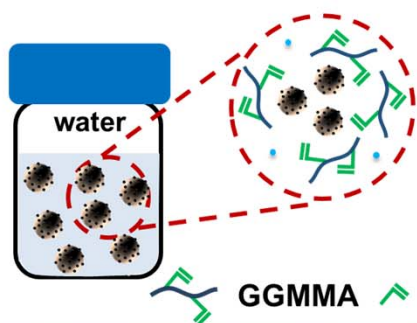
- spherical shape of AgNPs and hybrid LNP@Ag nanosphere (TEM and SEM)
- about 40 wt% metallic silver is present in LNP@Ag



# Biomass-based resin for DLP printing

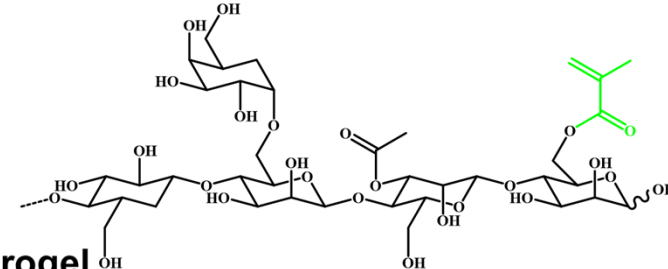
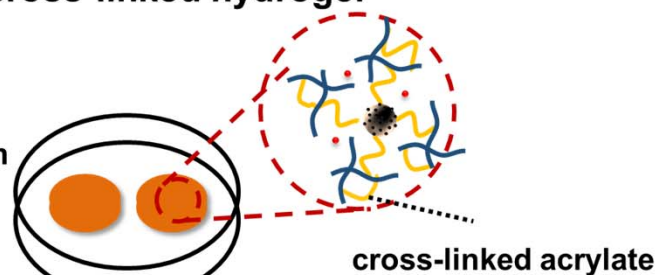
- UV cross-linkable polysaccharide-galactoglucomannan methacrylates (GGMMA)
- digital light processing (DLP) printing, 405 nm wavelength

(a) GGMMA/LNP@Ag resin

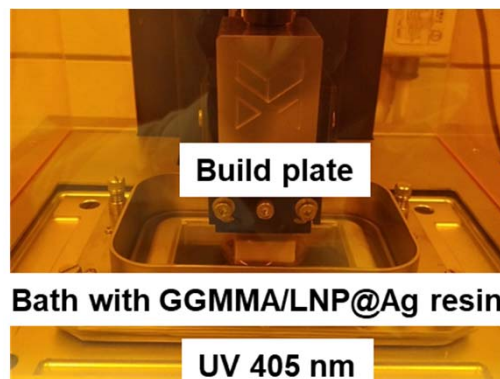


(d) UV cross-linked hydrogel

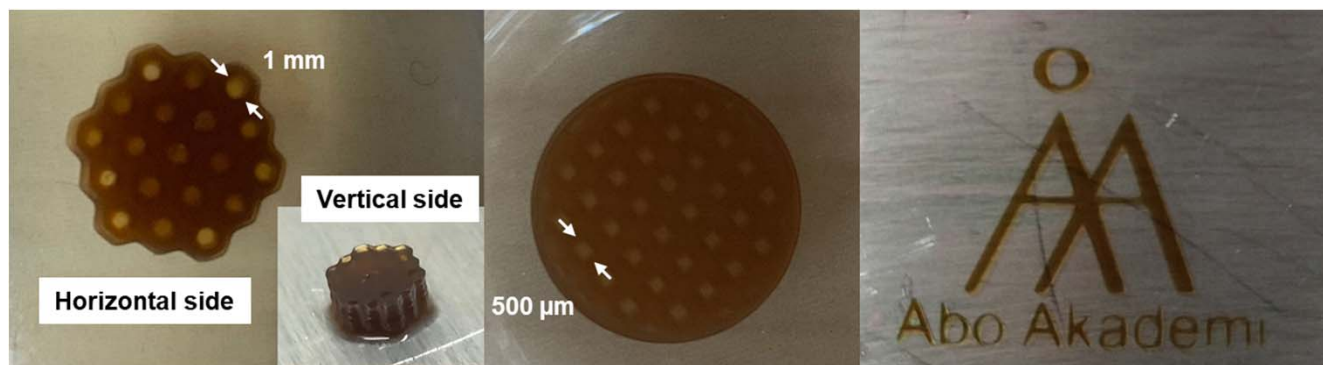
UV source: 405 nm  
DLP printing



# DLP printing



Outputs (e.g., porous hydrogels)

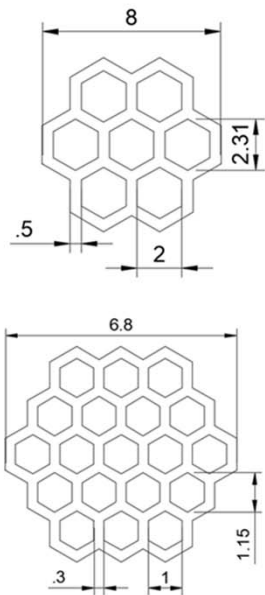


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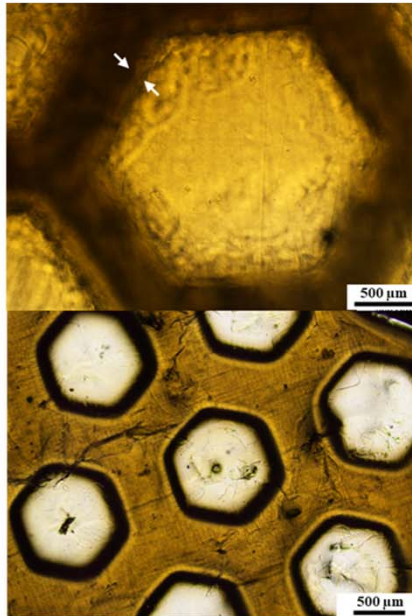


# DLP printing-printability

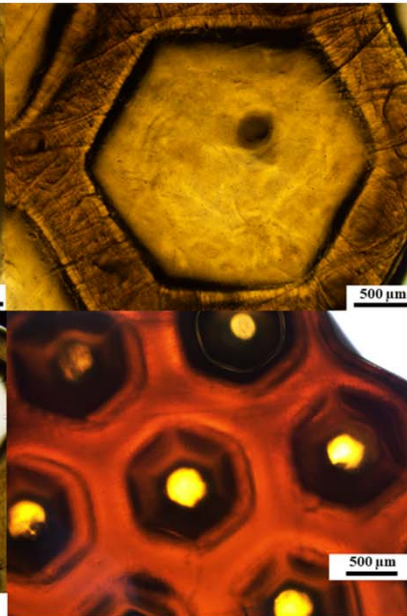
**Objects**



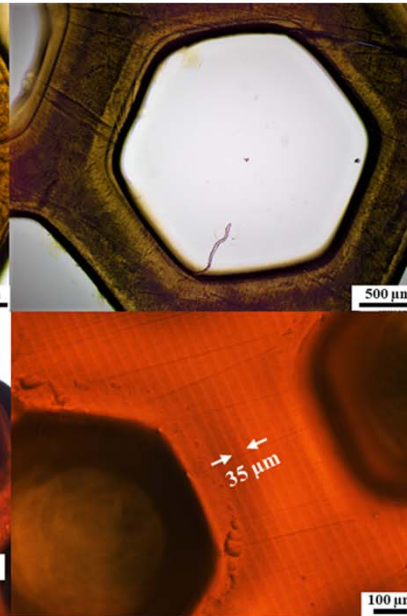
**GGMMA**



**GGMMA/0.1LNP**

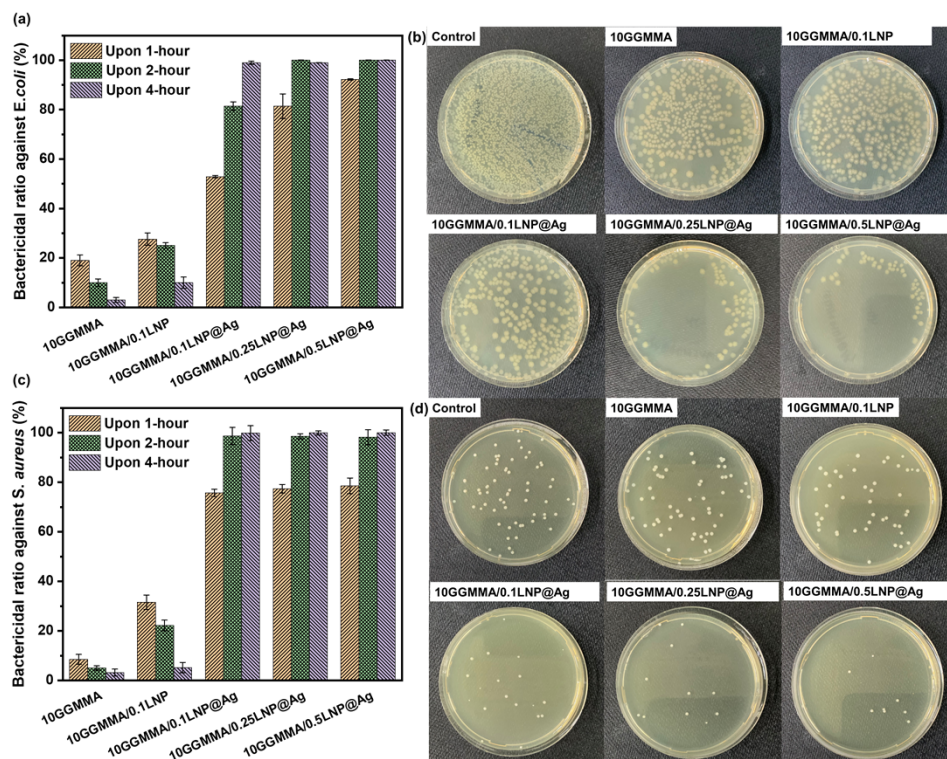


**GGMMA/0.1LNP@Ag**



- LNP@Ag improved the DLP printing fidelity of GGMMA polysaccharide
- LNP@Ag works as a “light-absorber” to the GGMMA/LNP resin

# Antimicrobial property of hydrogel



- strong antibacterial activities against both *E. coli* and *S. aureus*
- the embedded AgNPs on LNPs endow the antibacterial activities to the polysaccharide-based hydrogels



# Conclusions

- The bacteria-derived alkaliphilic laccase extensively catalyzed the oxidation and polymerization of AL fractions
- The inert property of laccase-treated lignin endows alkali resistance to the LNP and thus could be served as a functional support for *in situ* Ag reduction
- This work provides a new frontier in lithography-based DLP printing research focusing on natural-polymer-based resin with good structural stability and printing fidelity

# Acknowledgement



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