

RESEARCH ARTICLE

3D printing of aligned cellulose nanofiber hydrogels for enhanced AuNP-based SERS sensing

Supplementary Files

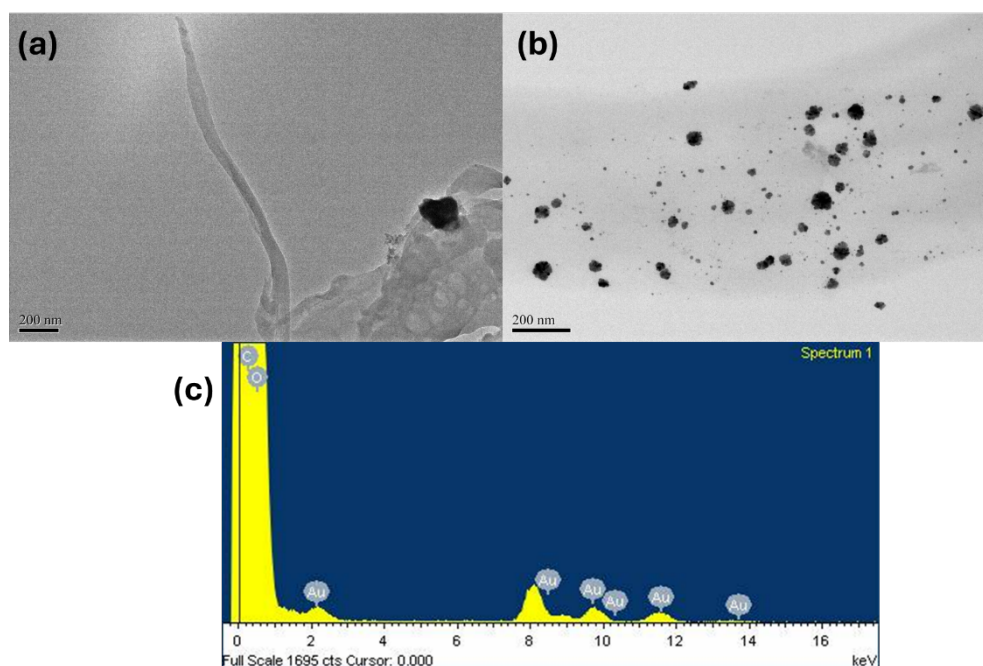


Figure S1. (a) TEM images of pristine CNFs, (b) AuNP-decorated CNFs, and (c) EDS analysis confirming the presence of AuNPs on CNFs
Abbreviations: AuNP: Gold nanoparticle; CNF: Cellulose nanofibers; EDS: Energy dispersive X-ray spectroscopy; TEM: Transmission electron microscopy.

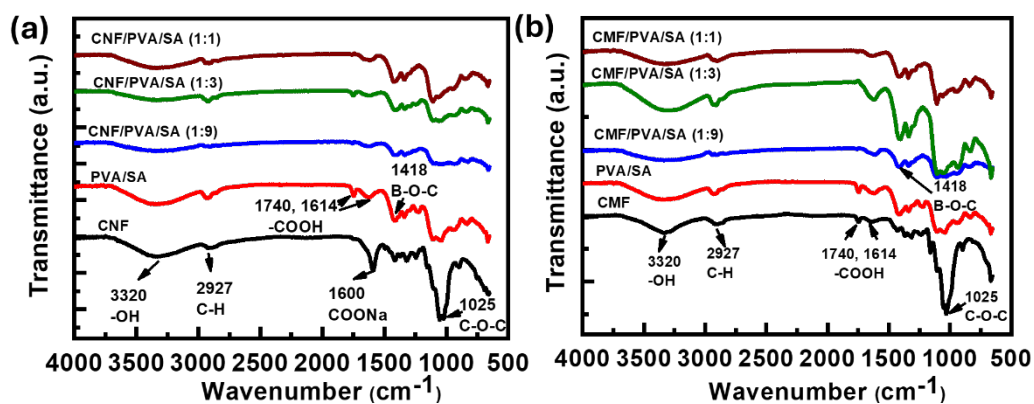


Figure S2. ATR-FTIR spectra of CF/PVA/SA hydrogels with varying fiber loadings: (a) CNF-based hydrogels and (b) CMF-based hydrogels
Abbreviations: ATR: Attenuated total reflection; CF: Cellulose fibers; CMF: Cellulose microfibers; CNF: Cellulose nanofibers; FTIR: Fourier transform infrared spectroscopy; PVA: Poly(vinyl alcohol); SA: Sodium alginate.

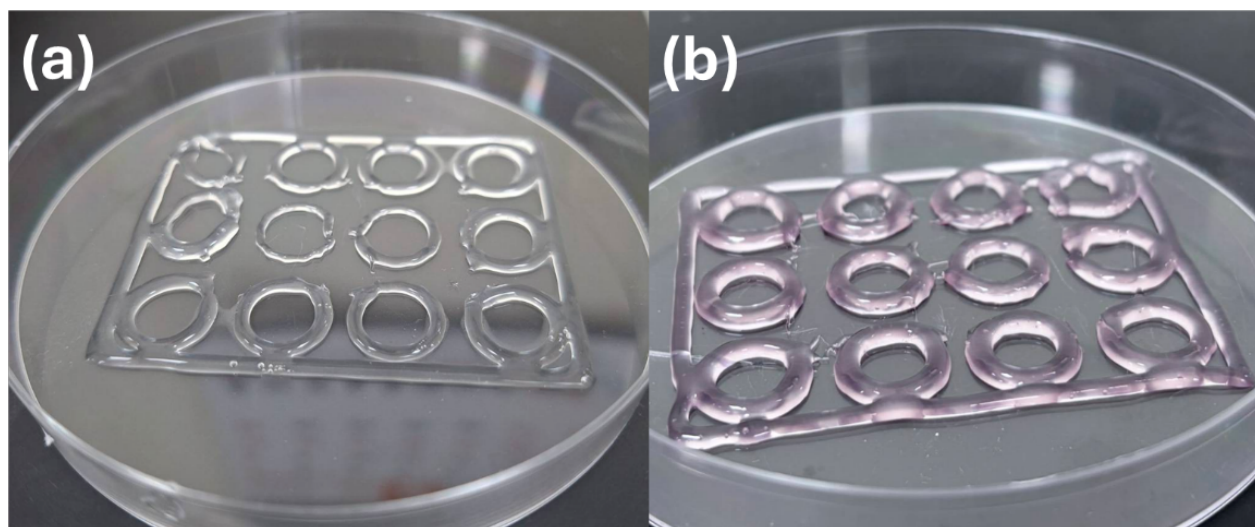


Figure S3. Photographs of 3D-printed hydrogel structures: (a) pristine hydrogels and (b) gold nanoparticle (AuNP)-incorporated composite hydrogels

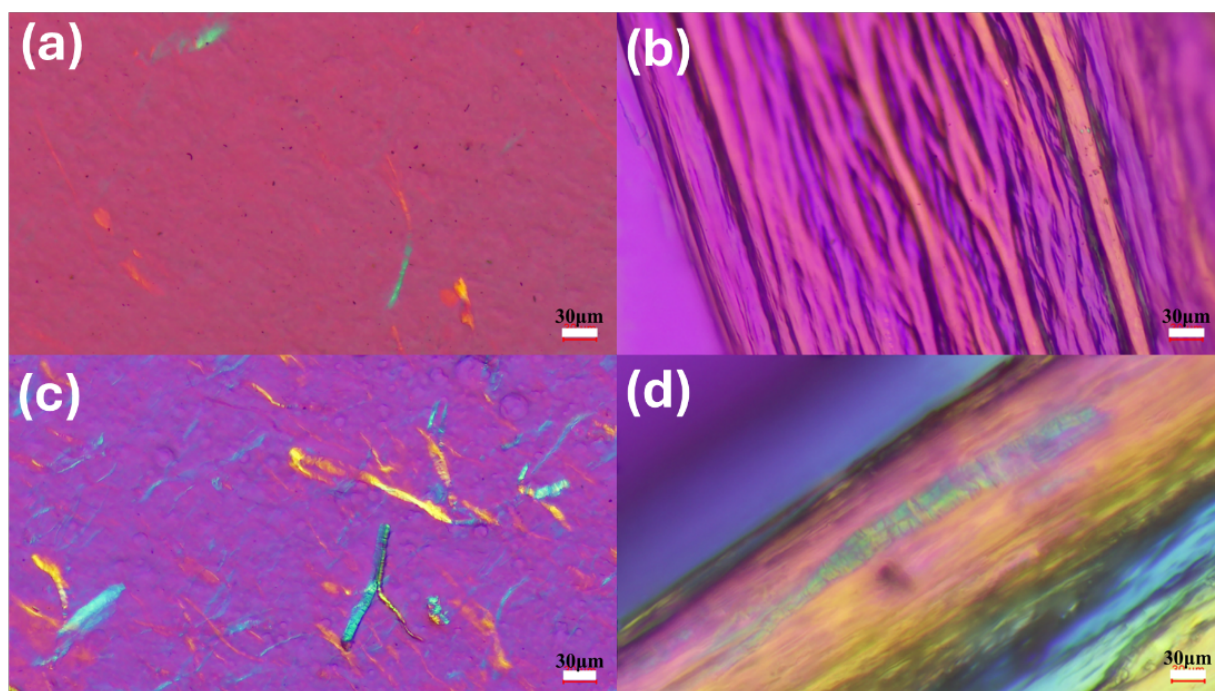


Figure S4. Polarized optical microscopy images illustrating shear-induced alignment. (a, b) Solution-cast film (a) and 3D-printed filament (b) of AuNPs/CNF/PVA/SA hydrogels. (c, d) Solution-cast film (c) and 3D-printed filament (d) of AuNPs/CMF/PVA/SA hydrogels. The images reveal a distinct transition from random fiber distribution in cast films to directional orientation in printed structures.

Abbreviations: AuNPs: Gold nanoparticles; CMF: Cellulose microfibrils; CNF: Cellulose nanofibers; PVA: Poly(vinyl alcohol); SA: Sodium alginate.

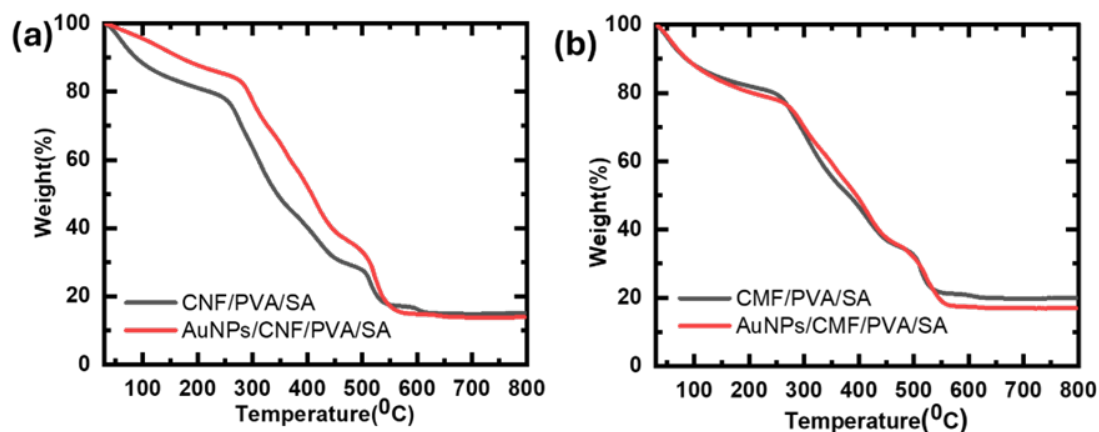


Figure S5. Comparative TGA curves illustrating the effect of AuNP incorporation. Weight loss profiles of (a) CNF-based hydrogels and (b) CMF-based hydrogels. The black lines represent the pristine hydrogels, while red lines indicate the corresponding AuNP-loaded composites.

Abbreviations: AuNPs: Gold nanoparticles; CMF: Cellulose microfibrils; CNF: Cellulose nanofibers; PVA: Poly(vinyl alcohol); SA: Sodium alginate; TGA: Thermogravimetric analysis.

Table S1. Comparison of the SERS performance of PVA-based hydrogel and film systems

| Material | Analyte | Detection Range | LOD | Ref. |
|------------------|-----------|--------------------------|------------------------|----------------------------|
| AuNPs/C-CNF/PVA | R6G | 10^{-5} M– 10^{-8} M | 7.9×10^{-8} M | 14 (<i>in main text</i>) |
| PVA–AgNPs | R6G | 10^{-2} M– 10^{-5} M | 10^{-5} M | S1 |
| S-CNF–AgNPs/PAA | Urea | 10^{-4} M– 10^{-8} M | 6.3×10^{-5} M | S2 |
| | Uric acid | 10^{-4} M– 10^{-8} M | 4.0×10^{-6} M | |
| AgNPs–TOCNF/PAAM | R6G | 10^{-2} M– 10^{-6} M | 5×10^{-8} M | S3 |
| AuNPs/CF/PVA/SA | R6G | 10^{-8} M– 10^{-4} M | 10^{-6} M | This work |

Abbreviations: AgNPs: Silver nanoparticles; AuNPs: Gold nanoparticles; C-CNF: Carboxylated cellulose nanofibers; CF: Cellulose fibers; C-PAA: Crosslinked poly(acrylic acid); PAAM: Poly(acrylamide); PVA: Poly(vinyl alcohol); S-CNF: Sulfonated cellulose nanofibers; SA: Sodium alginate; SERS: Surface-enhanced Raman scattering; TOCNF: TEMPO-oxidized cellulose nanofibers.

References

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