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# Time optimized genipin chitosan aerogels for catalytic applications

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## INTRODUCTION & AIM

Biopolymer aerogels offer sustainable supports for metal nanoparticle catalysts due to their high porosity, low density, and tunable chemistry (reported in sol–gel and polysaccharide aerogel literature [1] [2]. However, their catalytic performance is strongly governed by structural stability, crosslinking, and mass transfer properties.

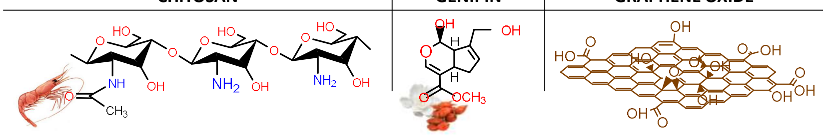
This work investigates a series of Au-loaded chitosan aerogels with controlled genipin crosslinking and GO reinforcement and assess their catalytic activity using the **model catalytic reduction of 4-nitrophenol**.

## METHOD

Genipin-crosslinked chitosan aerogels were fabricated by varying the crosslinking time, followed by freezing in polystyrene molds and freeze-drying to obtain stable porous network.

Sample formulation:

- **CS_1:** Pure chitosan (2.4%),
- **CS_2:** Chitosan + genipin(1.67%): 8 hours of crosslinking,
- **CS_3:** Chitosan + GO-reinforced(10%) + genipin: 8 hours of crosslinking
- **CS_4:** Chitosan + genipin : 24 hours of crosslinking
- **CS_5:** Chitosan + GO-reinforced(10%) + genipin: 24 hours of crosslinking

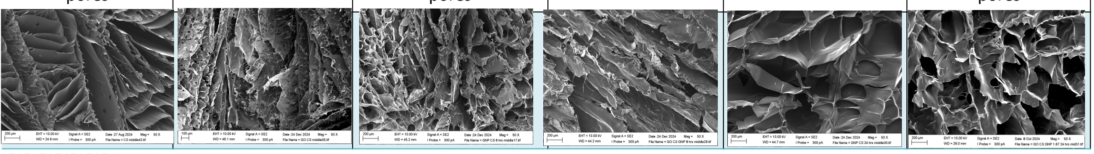



Au precursor was incorporated into each aerogel and reduced with $NaBH_4$ to form Au nanoparticles. Catalytic activity was monitored by UV–Vis spectroscopy at 400 nm, while morphology and composition were analyzed by SEM, FTIR, and XPS. Thermal and mechanical performances were evaluated using TGA/DTG and a universal testing machine, respectively.

## RESULTS & DISCUSSION

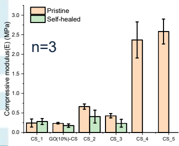
### Material characterization- Morphology, chemical structure, thermal and mechanical property

| CS_1 | GO(10%)-CS | CS_2 | CS_3 | CS_4 | CS_5 |
|---|---|---|---|---|---|
| Lamellar structure and poorly interconnected pores | Low-porosity structure with GO aggregation | Semi-interconnected structure and partially collapsed pores | Irregular pores and partial GO aggregation | Highly compact structure and very low pore connectivity | 3D porous network with larger interconnected pores |



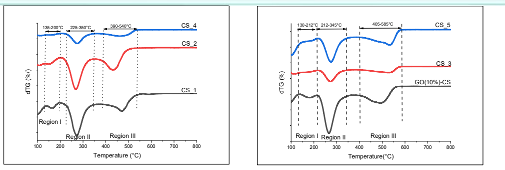
| | Uniaxial Compressive modulus [MPa] | | Single cycle |
|---|---|---|---|
| | Pristine ($E_p$) | Self healed ($E_h$) | Self healing efficiency($\eta_E$) (%) |
| CS_1 | 0.243 | 0.281 | 116 |
| GO(10%)-CS | 0.239 | 0.177 | 74 |
| CS_2 | 0.663 | 0.407 | 61 |
| CS_3 | 0.429 | 0.237 | 55 |
| CS_4 | 2.367 | - | 0 |
| CS_5 | 2.582 | - | 0 |

Compressive modulus healing efficiency $(\eta_E) = \frac{E_h}{E_p} * 100$




- Modulus(E) increases with increased crosslinking time.
- Single cycle self-healing efficiency of aerogel examined by comparing compressive modulus of pristine and post healing samples that involved manual cleaving and triggering healing with neutral water on cleaved surfaces shows that higher crosslinking time samples can not be repaired.

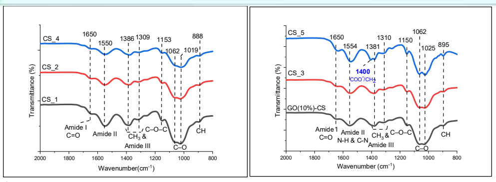
### DTG



**Region I: evaporation of adsorbed/bound water/ Region II: main degradation of the chitosan backbone/ Region III: decomposition of the carbonaceous residue.**

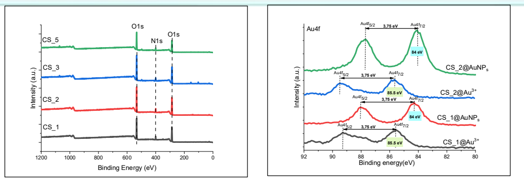
- Early and intense degradation peaks in GO(10%)–CS : indication of lower thermal stability.
- Reduced main peaks intensity in $CS_3$: evidence of moderate improvement in thermal stability.
- Degradation peaks shifted to higher temperatures in $CS_5$ : demonstration of the highest thermal stability.

### FTIR (crosslinking)



- Sharper and shifted Amide II band: evidence of genipin reacting with chitosan amine groups.
- Reinforced $CH_3$ and Amide III bands: more rigid and better-organized chitosan network.
- Unchanged glycosidic bands (1150–1060 and 895 $cm^{-1}$): chitosan polysaccharide backbone preserved.

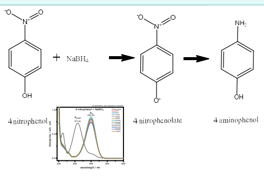
### XPS (Au loading)

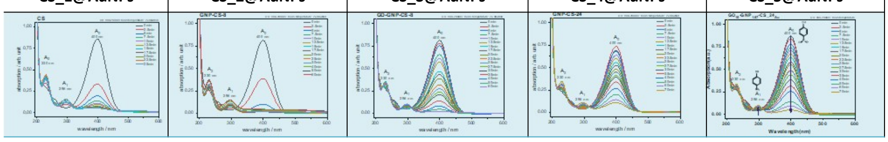


- Characteristic Au 4f spin–orbit doublet detected/ confirmation of gold incorporation in the aerogels.
- Shift of Au 4f peaks from higher to lower binding energy after $NaBH_4$: evidence of in-situ reduction of $Au^{3+}$.
- Appearance of Au $4f_{7/2}$ around ~84 eV: formation of metallic $Au^0$ nanoparticles.

### Catalytic study

- ✓ **Swelling Test:** GO(10%)-CS disintegrated → excluded from catalysis.
- ✓ **Au Loading:** Aerogels were immersed in $10^{-3}$ M $HAuCl_4 \cdot 3H_2O$ for Au3+ complexation.
- ✓ **AuNP Formation:** In situ reduction of $Au^{3+}$ inside the network.
- ✓ **Model Reaction:** Reduction of 4-nitrophenol to 4-aminophenol using $NaBH_4$ (UV–Vis monitored).CS_2 disintegration after 15 minutes




- Decrease of the 400 nm band with new peaks at ~300 and ~230 nm: confirmation of reduction of 4-nitrophenol to 4-aminophenol by all AuNP-loaded aerogels.
- Slower decrease of the 400 nm band in $CS_4$ & $CS_5$: reduced catalytic kinetics due to lower pore accessibility in the more densely crosslinked network.

## CONCLUSION

The study shows that crosslinking strongly dictates the structural and functional performance of chitosan-based aerogels. GO-only and weakly crosslinked samples disintegrated during swelling or catalysis, confirming insufficient network stability. Increasing genipin crosslinking time improved thermal and mechanical properties, with **CS_3, CS_4, and CS_5** showing the highest stability in aqueous conditions. However, all three exhibited slow catalytic reduction of 4-nitrophenol due to restricted diffusion and limited accessibility of Au active sites within their increasingly dense networks. Among them, **CS_3 provided the best overall compromise**, maintaining stability while retaining partial self-healing (~55%). **CS_4** became too rigid to heal, and **CS_5**, despite being the most structurally robust, showed the slowest catalytic response. The higher-crosslinked aerogels also demonstrated strong structural persistence after catalysis, indicating good potential for reuse. Overall, intermediate-to-high crosslinking improves stability and recyclability but limits catalytic efficiency, highlighting the need for pore and surface engineering to accelerate reaction rates without sacrificing durability.

## FUTURE WORK / REFERENCES

- Optimize GO dispersion and control pore morphology to reduce diffusion limitations and boost catalytic efficiency.
- Correlate Au loading, particle size and dispersion with catalytic performance and recyclability.
- Extend system to other environmental or reduction reactions.

[1] H. Yu, S. Oh, Y. Han, S. Lee, H. S. Jeong, and H.-J. Hong, 'Modified cellulose nanofibril aerogel: Tunable catalyst support for treatment of 4-Nitrophenol from wastewater', *Chemosphere*, vol. 285, p. 131448, Dec. 2021, doi: 10.1016/j.chemosphere.2021.131448.

[2] S. Ye, Y. Wang, B. Du, L. Cheng, L. Sun, and P. Yan, 'Recoverable sepiolite coated B-CoP/ cellulose hybrid aerogel as monolithic catalysts for hydrogen generation via NaBH4 hydrolysis', Chemical Engineering Journal, vol. 474, p. 145772, Oct. 2023, doi: 10.1016/j.cej.2023.145772.