Mechanochemical Synthesis of Chemically Stable Covalent Organic Frameworks Crafted on Cellulose Nanocrystals

Ramin Majidov[1*], Frederik Haase[2], Sandra Kaabel[1]

1 Department of Chemistry and Materials Science, Aalto University, 02150 Espoo, Finland; 2 Institute of Chemistry, Faculty of Natural Sciences II, Martin-Luther-Universität Halle-Wittenberg, 06120 Halle/Saale, Germany

**Corresponding author: ramin.majidov@aalto.fi*

Highlights

- Mechanochemical modification of CNCs
- Solvent-free synthesis of porous Covalent Organic Frameworks (COFs)
- Synthesis of novel, stable hybrid materials: CNC-COF

1. Introduction

Covalent organic frameworks (COFs) represent a promising class of crystalline porous materials known for their low density, high surface area, permanent porosity, and tunable structures [1]. Despite these appealing characteristics, their broader application remains constrained by limited mechanical strength and chemical instability, which hinder large-scale implementation [2-3]. In contrast, cellulose - the most abundant renewable biopolymer on earth, offers excellent chemical stability, mechanical robustness, low toxicity, and good processability [4]. In this work, we propose the development of hybrid materials by constructing COFs on modified cellulose nanocrystal (CNC) surfaces to enhance the overall stability of COF-based systems. Using a mechanochemical synthesis route, a solvent-free and environmentally friendly method, we were able to produce more stable, crystalline and porous CNC-COF hybrids rapidly at room temperature, avoiding the use of toxic organic solvents and prolonged reaction conditions at high temperatures typically required in conventional solvothermal synthesis.

2. Methods

All CNC modification experiments were carried out in a Retsch MM 400 mill while the synthesis of COFs and CNC-COF was performed in a Retsch MM2000 mill.

3. Results and discussion

Figure 1 represents the schematic representation of this work. Both COF and novel CNC-COF material displayed intense powder X-ray diffraction (PXRD) peaks at 2.6° (100), 4.5° (110), and 9.5° (210), signaling hexagonal symmetry. This close match underscores the structural fidelity of the epitaxial COF growth on the CNC substrate, where the interfacial nucleation preserves the hexagonal lattice parameters of the 2D COF sheets. Simulated AA-eclipsed (optimized: a=b=37.2 Å, c = 6.8 Å, γ = 120°) versus AB-staggered (a = b = 37.2 Å, c = 13.6 Å) structures showed experimental data matching eclipsed stacking structures. Nitrogen physisorption revealed very high BET surface areas of 1955 m^2/g and 1620 m^2/g further highlighting the porous architecture of these materials. Quantitative assessment via elemental analysis (C, H, N, S content) determined the CNC incorporation at approximately 22 wt.% in the CNC-COF hybrid. ATR-IR spectra evidenced that both samples displayed a strong imine C=N stretching band around, a definitive marker of successful Schiff-base polycondensation and COF network formation. Chemical stability tests exposed that pristine COF exhibited early degradation signs after cycle 5, with broadening and intensity loss of (100)/(110) reflections by cycle 7. CNC-COF in contrast, retained sharp COF structures through 7 cycles, with only some degradation by cycle 10 but keeping persistent crystallinity even after 10 cycles. The results will be presented in detail at the conference.

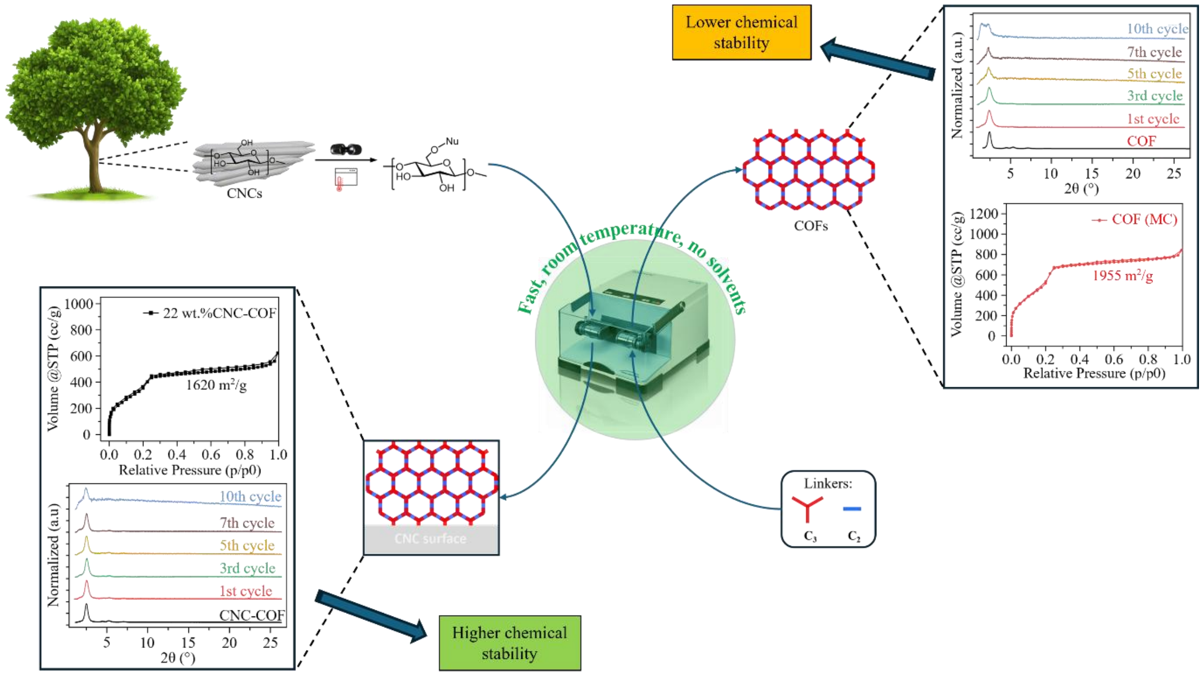

Figure 1. Schematic representation of this work: The results and short synthesis scheme of CNC-COF on the left; COF on the right.

4. Conclusions

This work demonstrates a significant advance toward overcoming the chemical stability limitations of COFs by constructing CNC-supported COF hybrids via a rapid, solvent-free mechanochemical route. The resulting CNC-COF materials preserve the high crystallinity, porosity, and hexagonal framework of the parent COF while incorporating ~22 wt.% CNCs. By combining enhanced robustness with a green, scalable synthesis method that avoids toxic organic solvents and high temperatures, this approach provides a promising pathway toward durable, sustainable COF-based materials for practical applications.

References

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Keywords

mechanochemistry, cellulose modifications, covalent organic frameworks.