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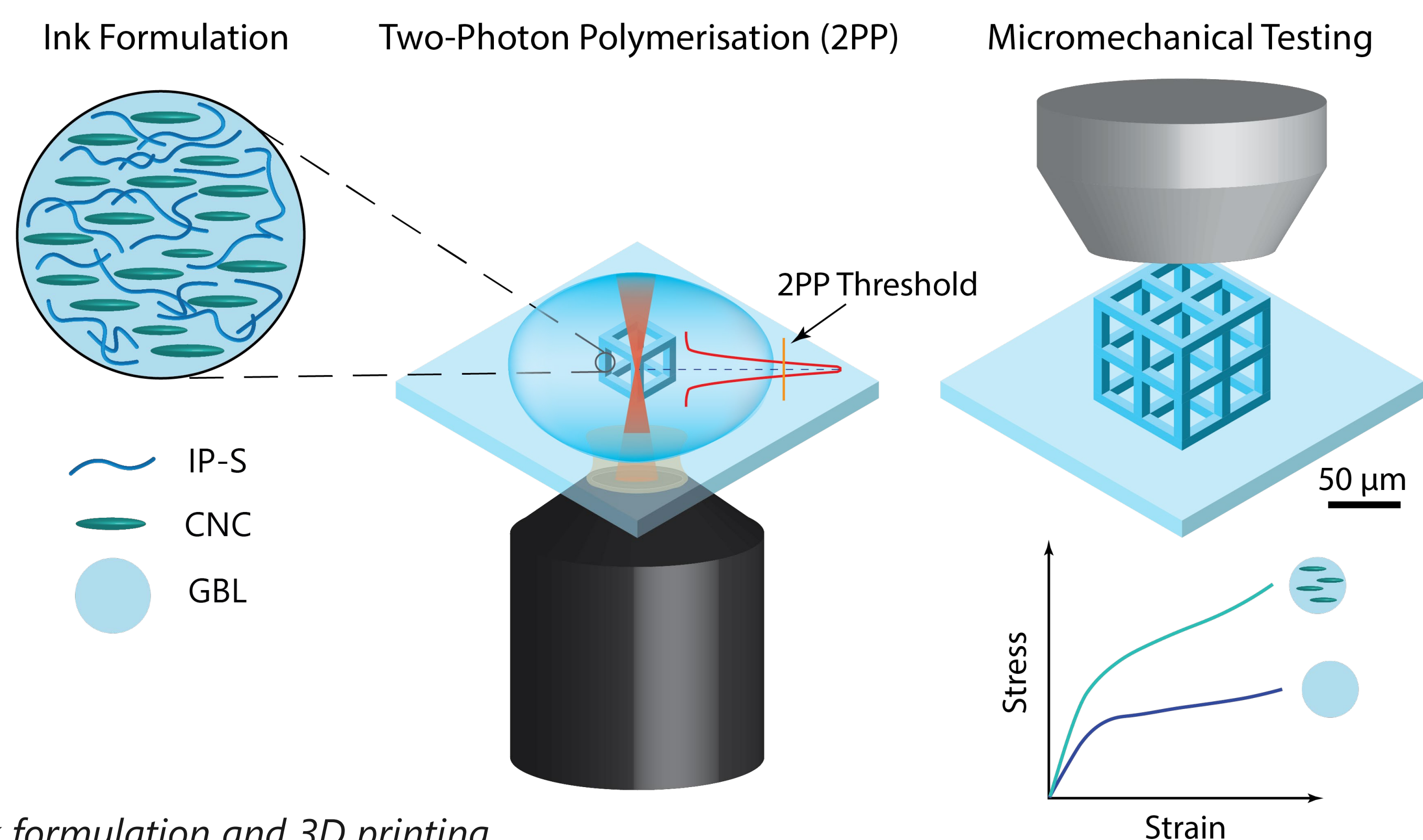
## Introduction and Objectives

Functional hierarchical metamaterials have gained importance in nearly all fields of engineering since they allow us to create well-controlled optical and structure-mechanical characteristics; desirable features, e.g. for bio- and tissue-engineering [1], photonics as well as novel microscale energy absorption devices. Two-photon polymerisation (2PP) is a promising nanofabrication technique that allows synthesizing structures up to the millimetre scale with sub-micrometre resolution [2]. Cellulose nanocrystals (CNC) are made of an abundant biopolymer. They are transparent in the visible and near-infrared range, possess outstanding mechanical properties and can be chemically functionalised. CNC ink has been used for macroscale 3D printing in the past [3]. However, the microscale fabrication with a CNC reinforced nanocomposite ink has not been achieved.

**Therefore we aimed to:**

- Fabricate a polymer based CNC ink for 3D 2PP printing of microscale architectures
- Explore how to tune the 3D printed structures mechanically with different CNC amount

## Materials and Methods



### Ink formulation and 3D printing

- CNC were suspended in an organic solvent (GBL) and mixed with a biocompatible and non-cytotoxic methacrylate-based photoresist (IP-S, Nanoscribe GmbH, Germany) to reach different CNC concentrations (4.5 wt% and 13 wt%)
- 2PP at laser powers 12.5mW-27.5mW was performed ensuring a reliable synthesis of micro-structures (micropillar, hexagon, cellular structure; minimum feature size 2 µm)

### Micromechanical testing and Raman microscopy

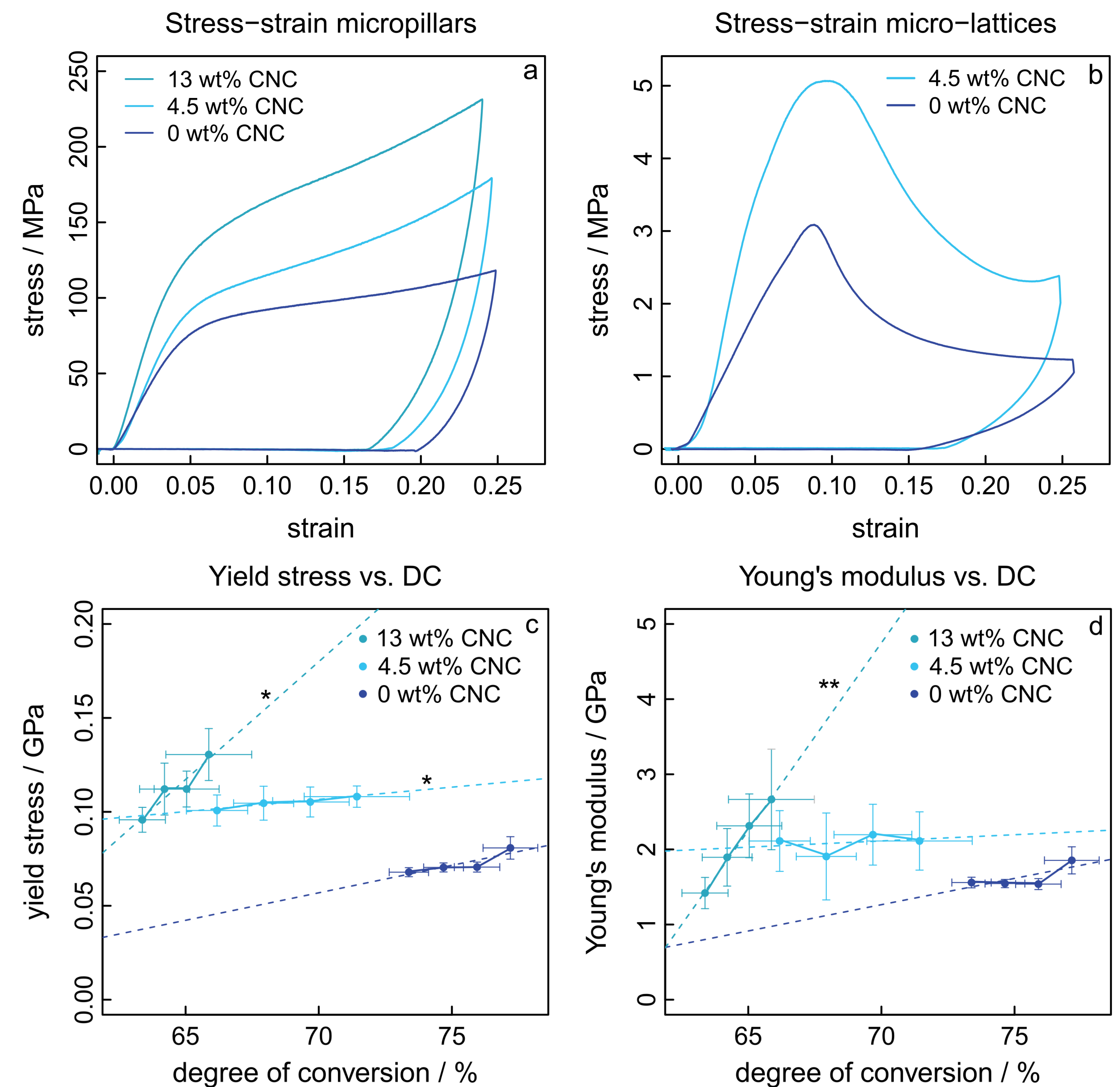
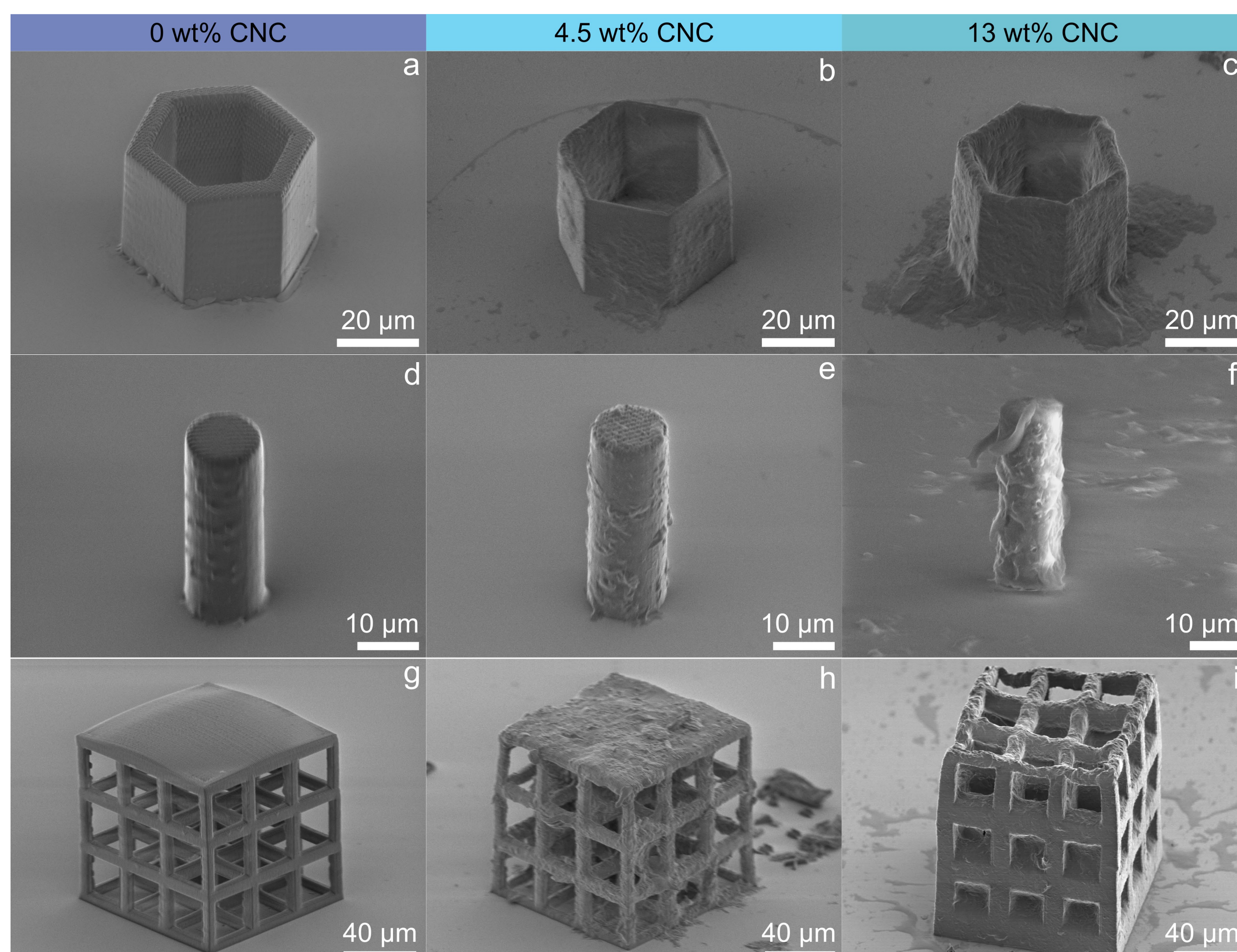
- Cellular structures (cubic dimensions  $\approx 92$ -102 µm) and micropillars (diameter  $\approx 13$  µm, aspect ratio  $\approx 3$ ) were uniaxially compressed inside an SEM using an *in situ* micro-indenter (Alemnis AG, Switzerland) at a quasi-static load (strain rate:  $10^{-3} \text{ s}^{-1}$ )
- Young's modulus, yield values and compressive strength were extracted from stress-strain curves, and the CNC influence was compared using a significance level of 0.05
- Raman spectra with a 785 nm laser were collected on the micropillars to determine the degree of conversion (DC) as a measure for the polymer matrix quality [4]

### Composite modelling

- Reuss and Voigt models for composites with two constitutive phases were used to predict the apparent stiffness accounting for a parallel or serial arrangement of CNC

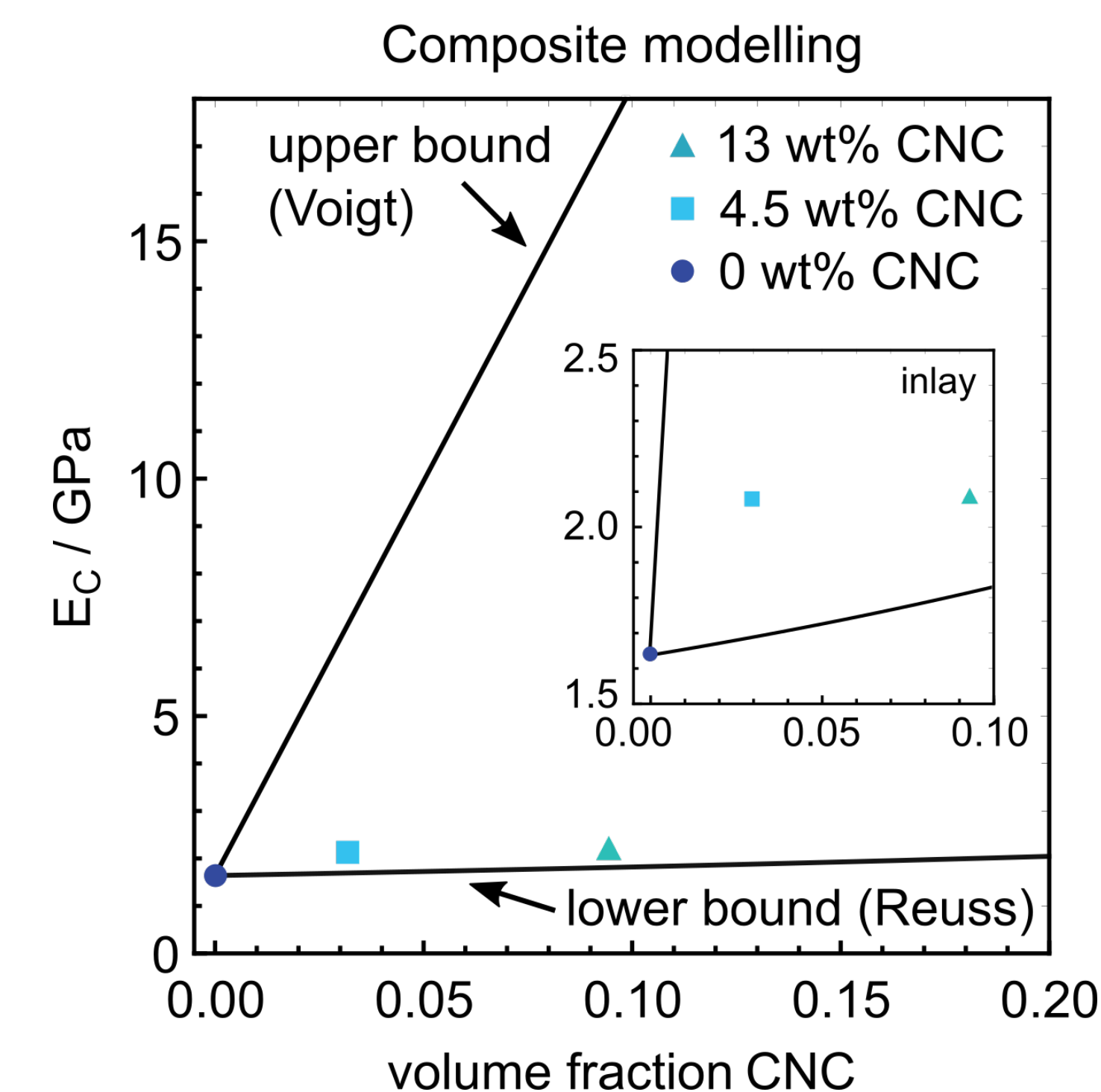
## Results

The 3D printing of the neat polymer and 4.5 wt% CNC/IP-S composites worked well while fibrous residues of CNC agglomerates were visible with increasing CNC content.



Adding CNC significantly increases yield stress and stiffness of both micropillars (30% for 4.5 wt% CNC; 70% for 13 wt% CNC) and cellular structures (100% for 4.5 wt% CNC).

The matrix quality depends on both the laser power and the CNC content. The maximum DC decreases with an increasing amount of CNC (81% for neat polymer, 74% for 4.5 wt% CNC and 69% for 13 wt% CNC) and increasing laser power. Yield stress and stiffness showed a positive correlation with the polymer matrix quality.



Comparing the different combinations of laser power and CNC content as well as the calculations for the degree of conversion (matrix quality), the best outcome was achieved for the 4.5 wt% CNC nanocomposites using a laser power of 17.5 mW for the 3D printing.

Composite modelling showed that the moduli  $E_c$  of both IP-S/CNC mixtures are close to the lower bound elastic moduli predicted by the model. This indicates that the CNC crystals were orientated mainly normal to the loading direction.

## Conclusion and Impact

- We show for the first time that it is possible to use two-photon polymerisation to print complex 3D microscale architectures with a nanocomposite CNC reinforced polymer matrix ink, and that their mechanical performance can be tailored.
- Adding only 4.5 wt% CNC enhances the mechanical properties of cellular structures by up to 100%, and those of 13 wt% CNC micropillars by 70%.
- Suitable combinations of laser induced polymerisation and amount of CNC reinforcements are essential to achieve a high matrix quality and enhanced mechanical performance while avoiding brittle failure.
- Composite modelling shows that CNC orientation plays an important role for the composites' stiffness.
- Our new insights into the 3D printing of complex microscale structures with a CNC reinforced polymer ink outline the potential in how to optimise the structure-mechanical performance of these promising architected materials.
- It allows us to improve their future design for applications including novel biomedical implants and microscale energy-absorption devices.

## References

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