Growing and Shaping Metal–Organic Framework Single Crystals at the Millimeter Scale

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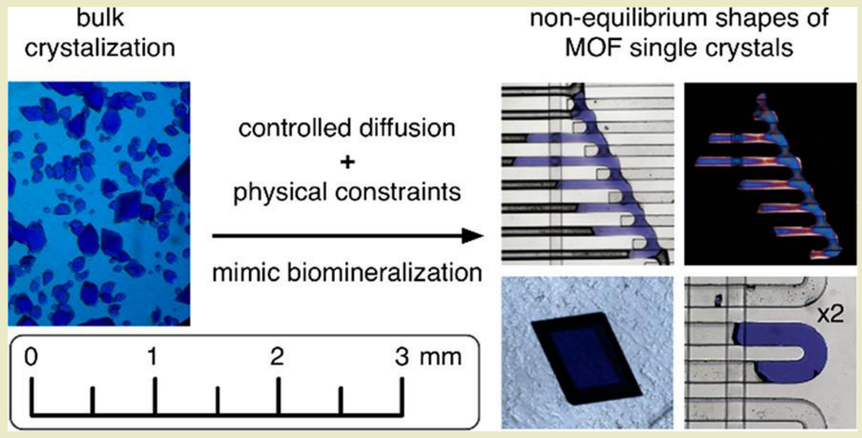
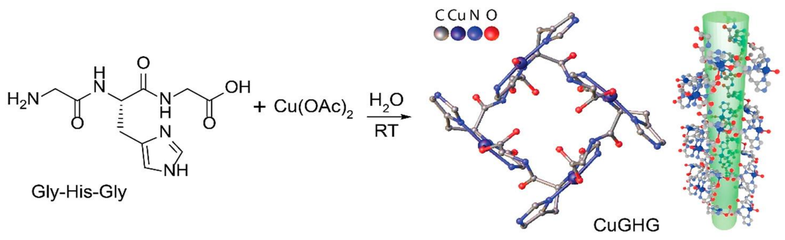
1. INTRODUCTION

- **Morphological control of crystals** is utterly important in reticular chemistry, especially as a fundamental strategy toward preparing functional materials of superior properties[1,2].
- In the realm of metal-organic frameworks (MOFs), previous endeavors primarily focus on shape manipulation at the nano- and microscale during bulk synthesis and subsequent processing at the mesoscale (e.g., incorporation into polycrystalline films, patterns, and composites) [3,4]
- A notable challenge persists in attaining a meticulous control over both the shape and size of macroscopic single crystals**.**
- Here we successfully demonstrated the spatial and morphological control of crystal growth from a **non-equilibrium state** through the utilization of a **microfluidic device**.
- Due to **low Grashof number condition** in microchannels, **homogenous growth** of peptide-based MOF - CuGHG was greatly promoted, resulting in formation of **well-shaped single crystal at millimeter scale.**

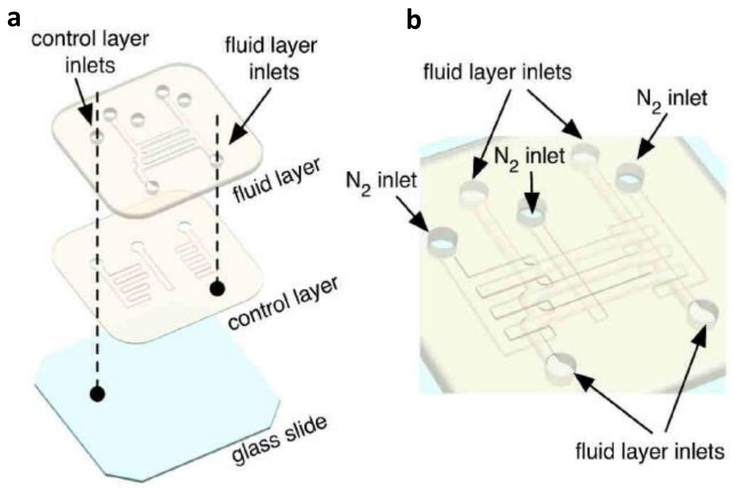


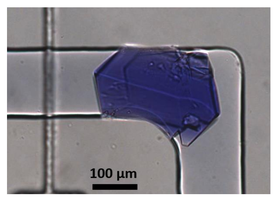
2. METHODOLOGY

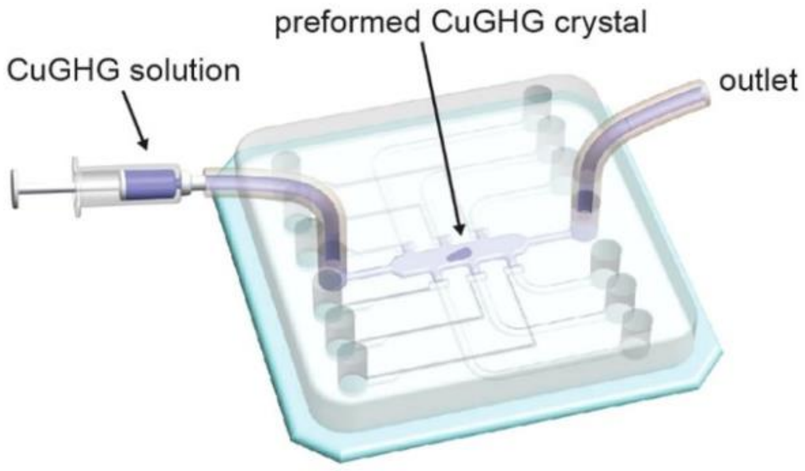
A. Preparing CuGHG solution



B. Fabrication of PDMS microfluidic chip



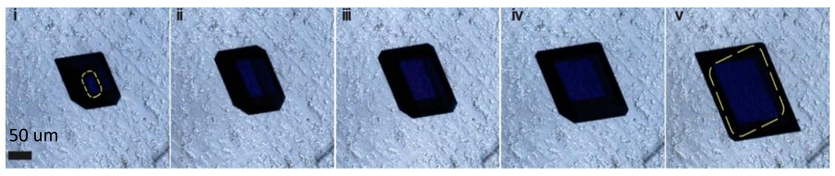




- Micro scale dimension enables **advection to be minimized** and allow the MOF solution to be stabilized and slowly transition from non-equilibrium to equilibrium state, resulting in homogeneous crystal growth.
- Due to **template effect** of microchannel, CuGHG crystal takes shape of channel it is confined in. We can tailor the size and shape of the microchannel to obtain desired size and shape of the crystal.
- CuGHG single crystals can **shrink and regrow** in response to laser-induced damage.

C. Confined growth of CuGHG crystal in microchamber

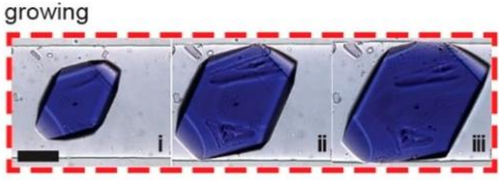
2D flat morphology



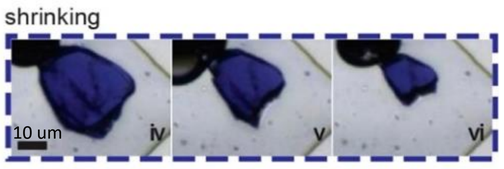
3D cylinder morphology

laser-induced damage

growing



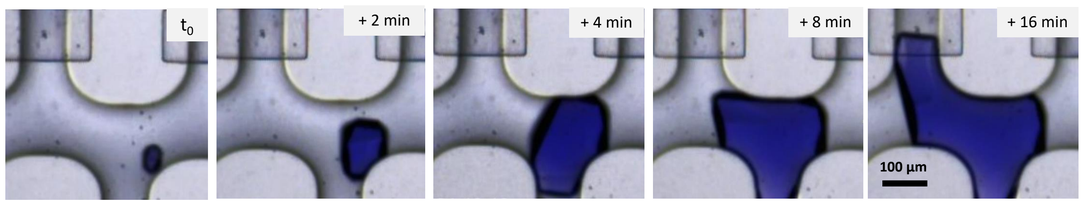
shrinking



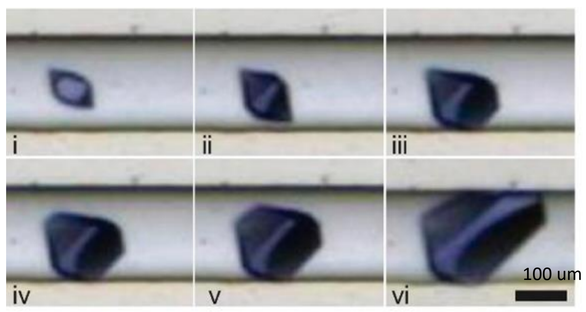
3. RESULT

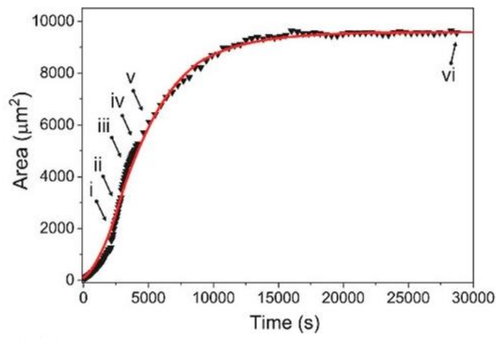
CuGHG crystal were grown and shaped using different microchambers

a

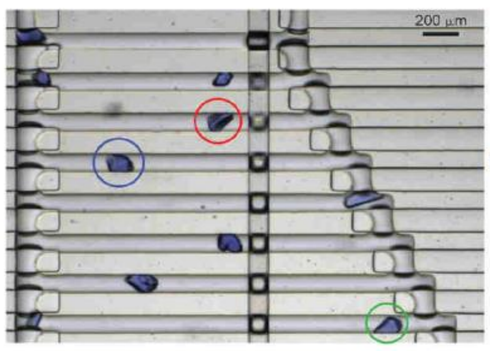


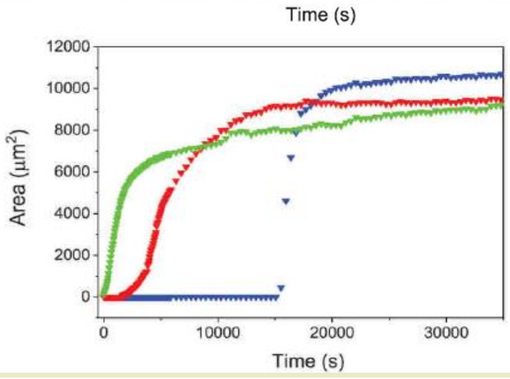
b





c





4. CHARACTERIZATION

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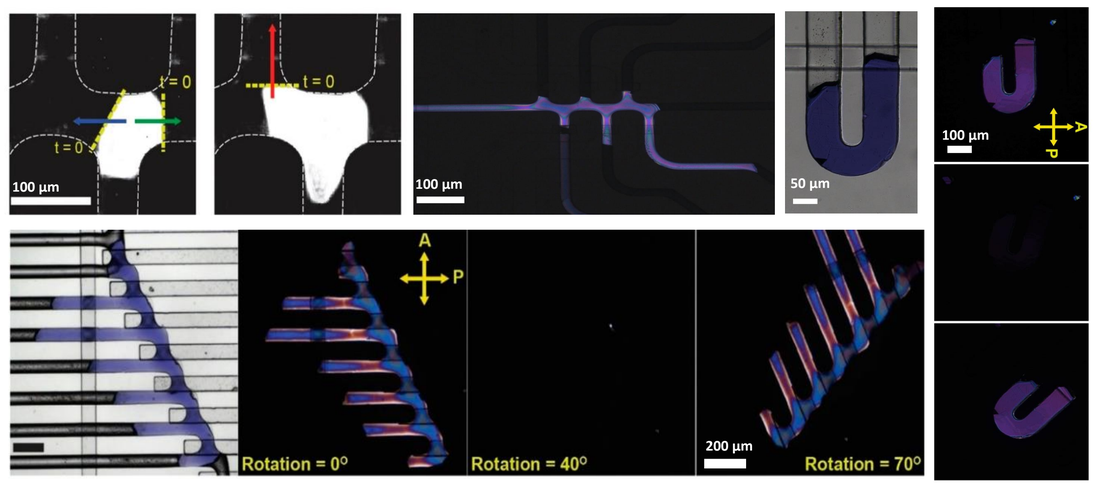

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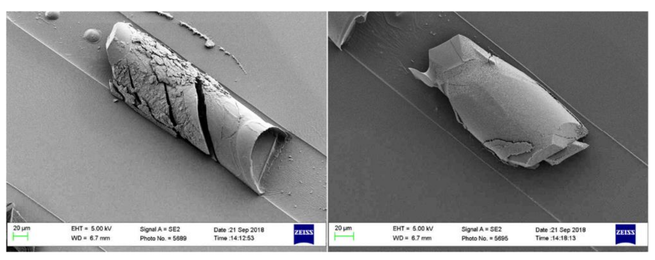

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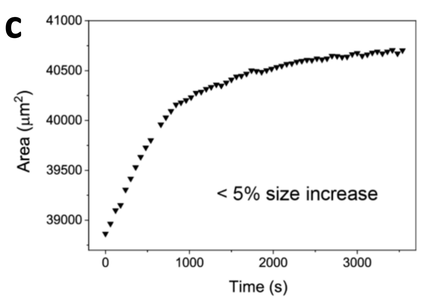

a) CuGHG crystals grown from microchambers are confirmed to be single crystals under cross polarizer. b) SEM images of selected CuGHG crystals c) In absence of flow, CuGHG crystal shows a non-linear growth profile approaching a plateau, which corresponds to a percentage increase of size as small as 5%

5. CONCLUSION

- Here we successfully demonstrated the **spatial and morphological control** of crystal growth at **the millimeter scale from a non-equilibrium state** through the utilization of a **microfluidic device**.
- Within an advection-free microenvironment of microchamber, peptide-based MOF – CuGHG can be grown homogeneously and continuously as a consequence of a diffusion-controlled supply of precursors.
- We can tailor the size and shape of the microchannel to obtain the size and shape of the crystal.
- Regrowth or shrinkage of the crystals after laser-induced damage demonstrated the stability and mechanical strength of the crystal.
- This work helps expanding the precise control over tailoring shape and size of different material classes for specific applications

References

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Acknowledgement

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