Customised Nanostructured Inorganic Materials via Microphase Separation 3D Printing

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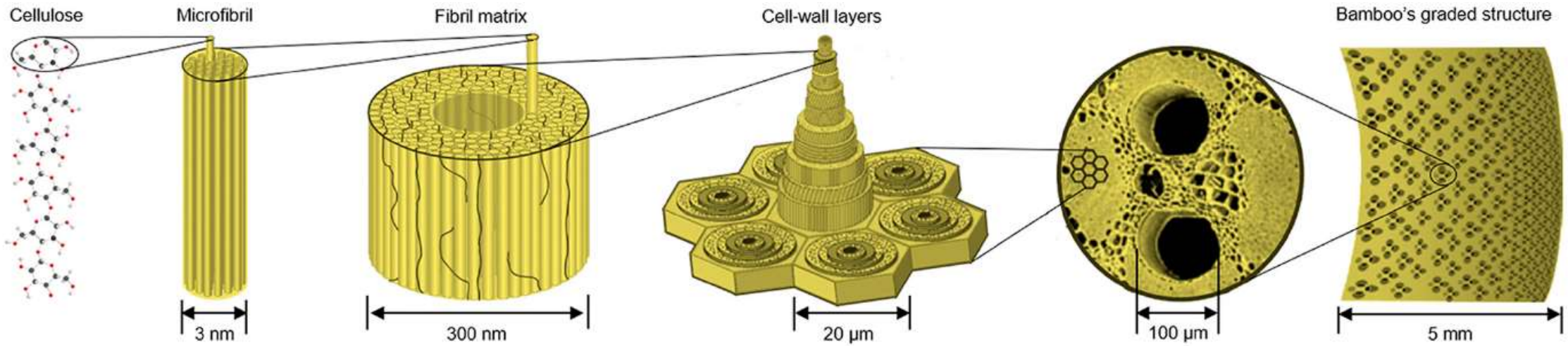
Insights derived from nature

Coaxial layered



100 nm — 100 µm — > 0.1 mm

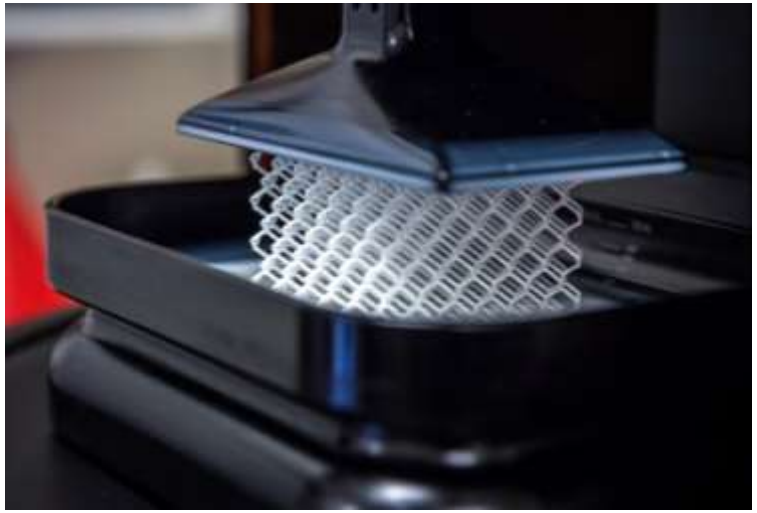
Nanoscale — Microscale — Macroscale

1. Studart, A. R., Towards High-Performance Bioinspired Composites. *Adv. Mater.* **2012**, 24, 5024–5044.
2. Wegst, U. G. K. et al. Bioinspired structural materials. *Nat. Mater.* **2015**, 14, 23-36.
3. Wei, J. et al. Bioinspired Additive Manufacturing of Hierarchical Materials: From Biostructures to Functions. *Research*. **2023**; 6:0164.

Can we mimic natural materials' structuration in synthetic materials using engineering and chemical approaches?

Top-down

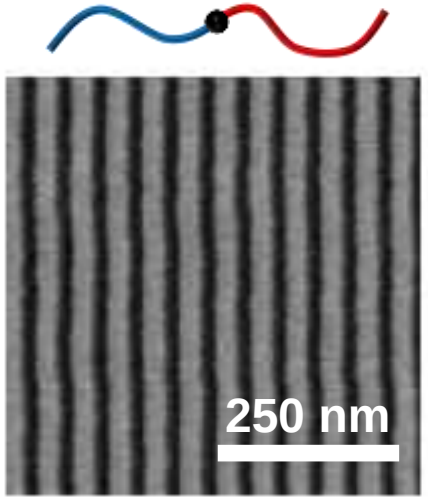
Stereolithography 3D printing

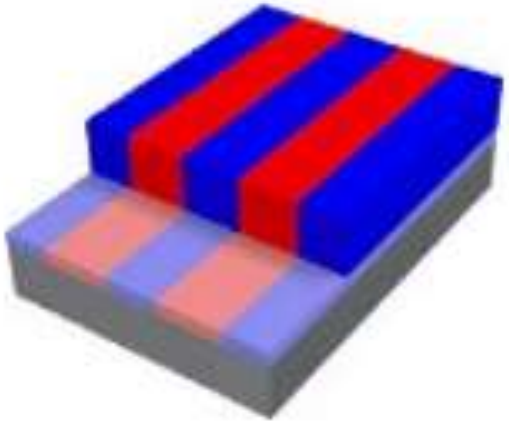


- ✓ High automation
- ✓ Accurate control over shape
- ✓ Geometrical Flexibility

Bottom-up

Block copolymer self-assembly

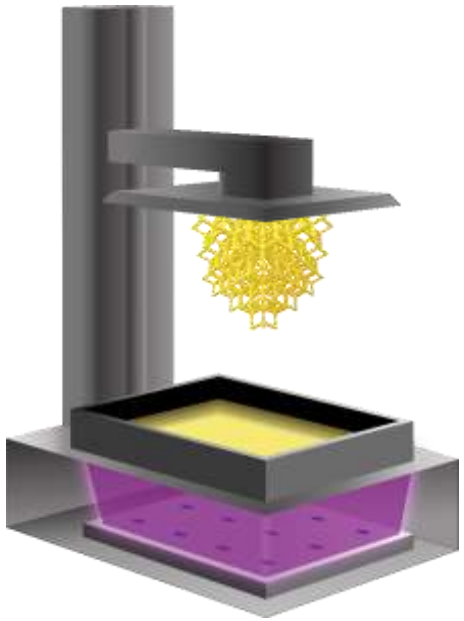


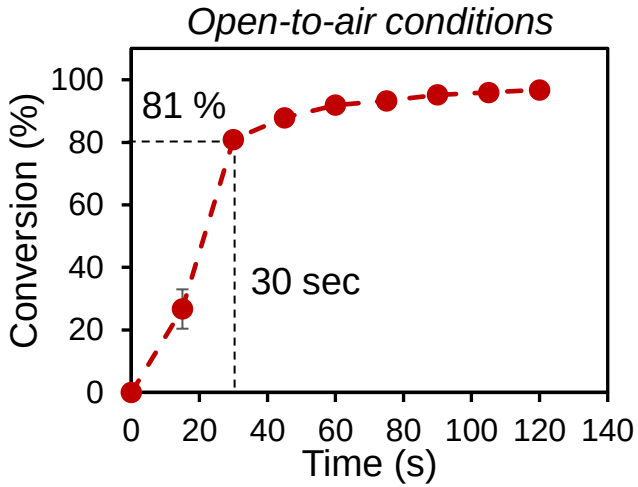


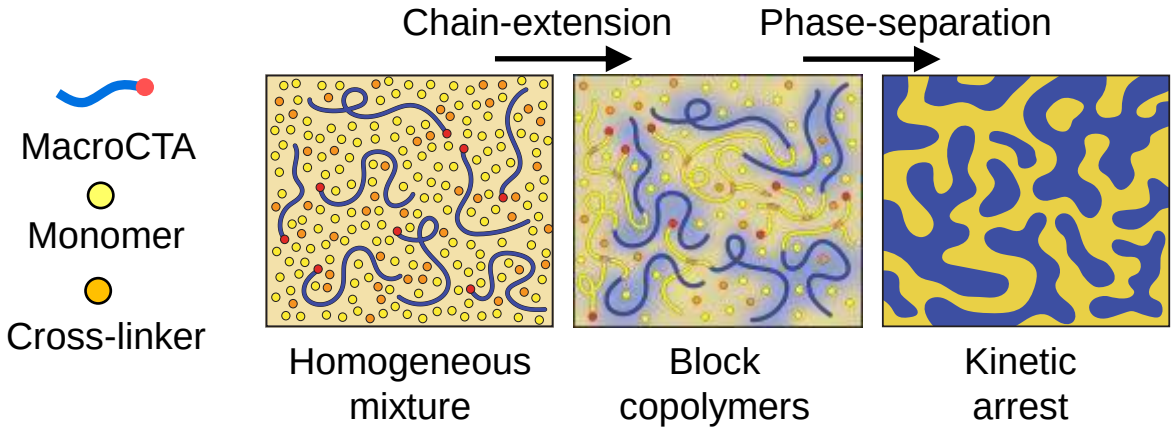
- ✓ Access to ultra-small features
- ✓ Nanoscale precision
- ✓ Choice of functionality

Our platform technology: PIMS 3D Printing

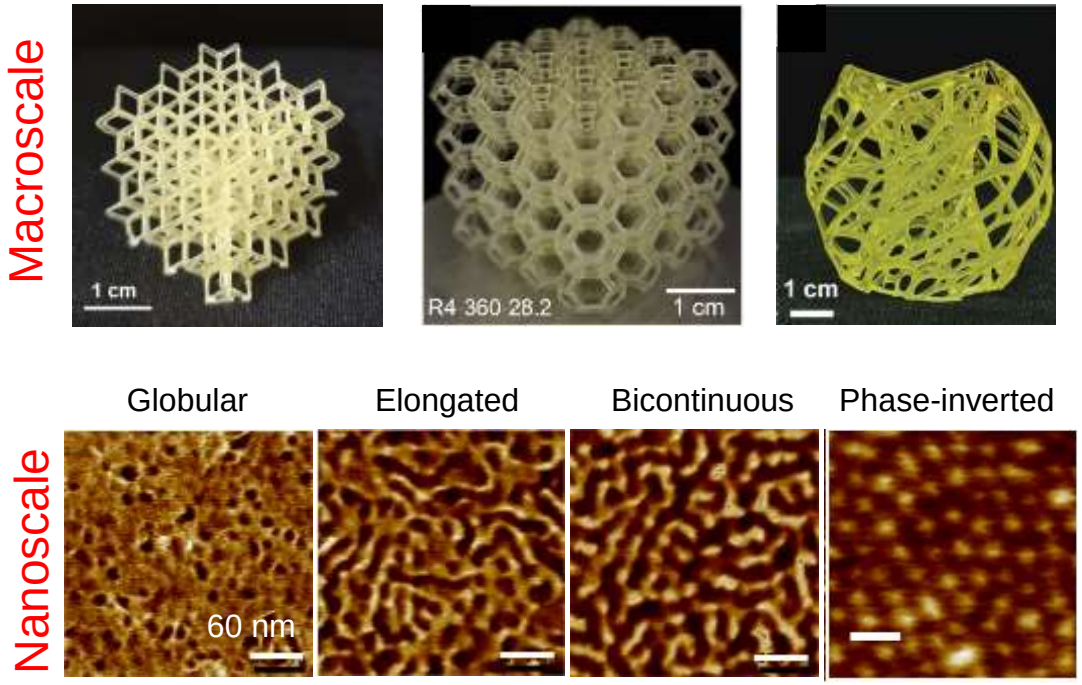
Design

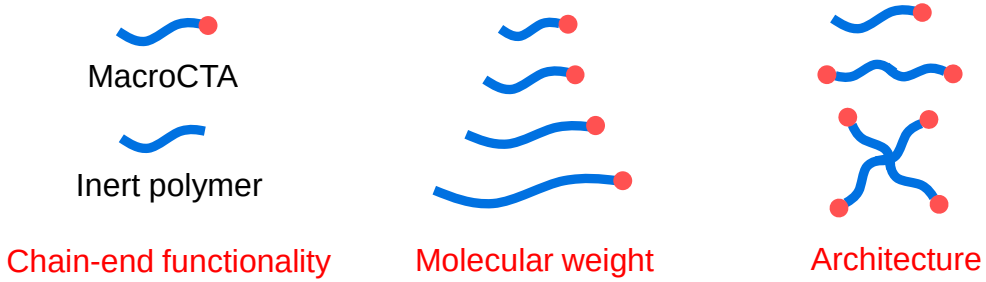






Experiment



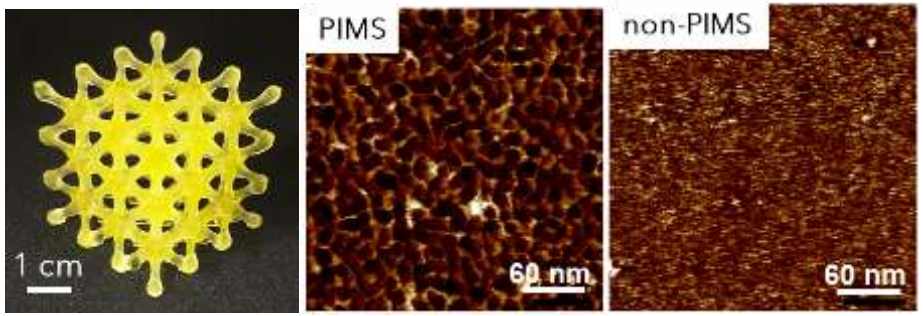


1. Seo, M. and Hillmyer, M. *Science* **2012**, 336 (6087), 1422. **2.** Bobrin, V. A., Lee, K., Zhang, J., Corrigan, N., Boyer, C. *Adv. Mater.* **2022**, 34 (4), 2107643. **3.** Bobrin, V. A., Yao, Y., Shi, X., Xiu, Y., Zhang, J., Corrigan, N., Boyer, C. *Nat. Commun.* **2022**, 13 (1), 3577. **4**. Shi, X., Bobrin, V. A., Yao, Y., Zhang, J., Corrigan, N., Boyer, C. *Angew. Chem. Int. Ed*. **2022**, 61, e2022062.

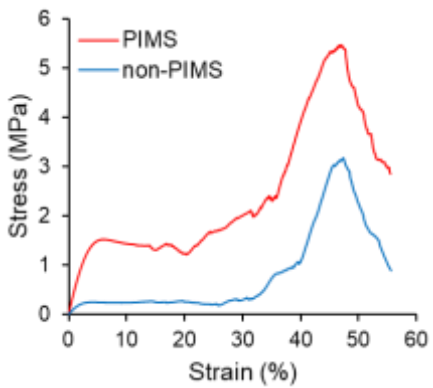
Impact of PIMS 3D Printing

Our approach is ***materials-versatile***, allowing us to prepare a rich variety of nanostructured 3D printed objects with various properties

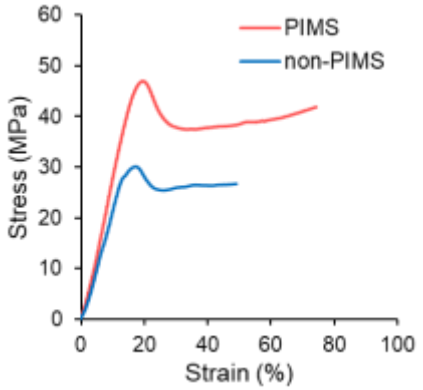
Multi-materials with enhanced mechanical properties



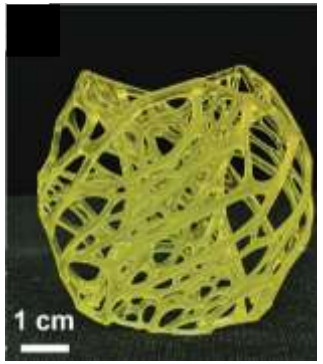
Compression

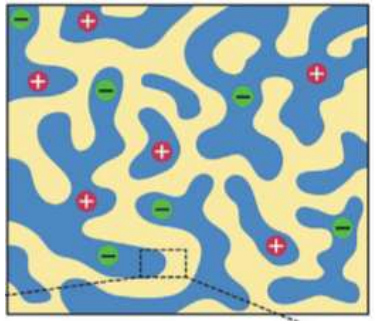


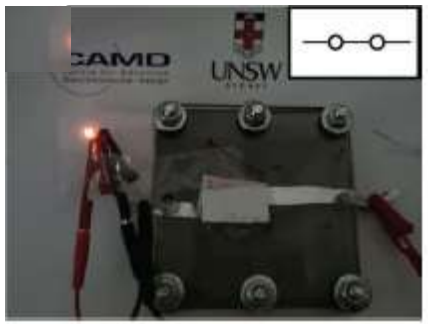
Tensile



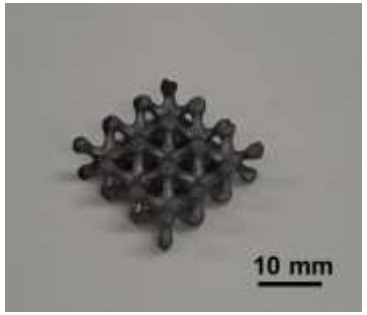
Mechanically robust solid polymer electrolyte

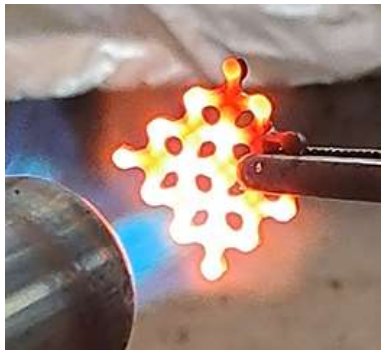






Customised nanoporous inorganic materials





1. Bobrin, V. A., Lee, K., Zhang, J., Corrigan, N., Boyer, C. *Adv. Mater.* **2022**, 34 (4), 2107643. **2.** Bobrin, V. A., Yao, Y., Shi, X., Xiu, Y., Zhang, J., Corrigan, N., Boyer, C. *Nat. Commun.* **2022**, 13 (1), 3577. **3**. Lee, K., Shang, Y., Bobrin. V. A., Kuchel, R., Kundu, D., Corrigan, N., Boyer, C. *Adv. Mater.* **2022**, 34, 2204816. **4**. Bobrin, V. A., Hackbarth, H. G., Yao, Y., Bedford, N. M., Zhang, J., Corrigan, N., Boyer, C. Customized Nanostructured Ceramics via Microphase Separation 3D Printing. *Adv. Sci.* **2023**, 2304734.

Applications of polymer-derived inorganic materials

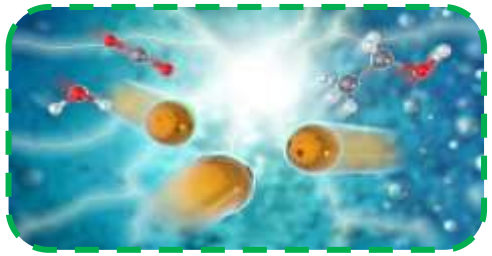
Advanced materials

UHT coating

Stealth tech

Ballistic protection

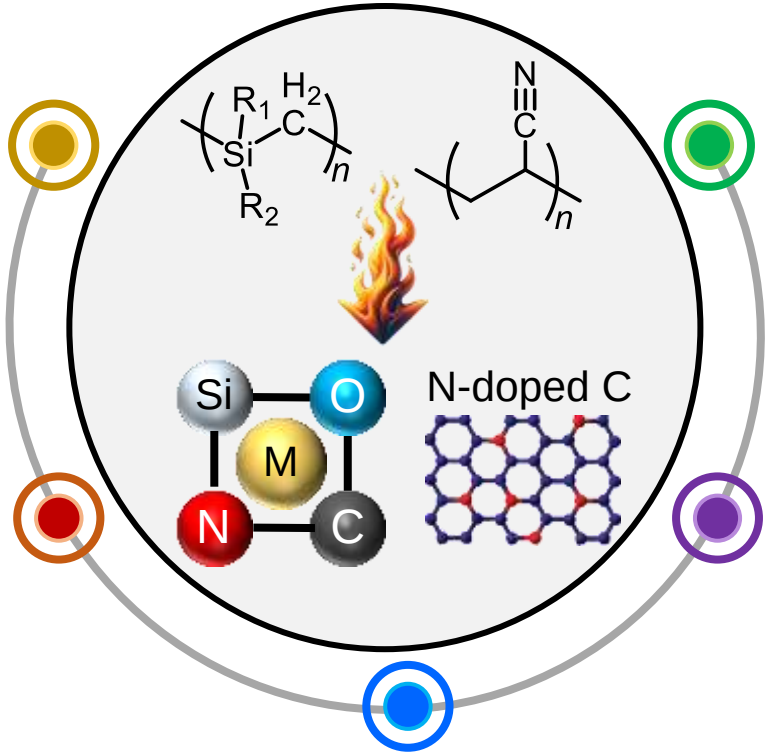
Catalysis



Catalyst support

Hydrogen production

Biomass conversion

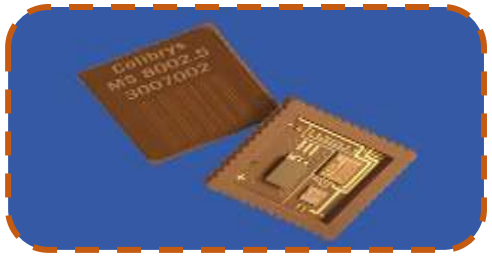


Electronics

MEMS

Microarray

Piezoelectric



Energy storage

Supercapacitors

Parts in batteries

Electrode separator

Pollution control

Membranes

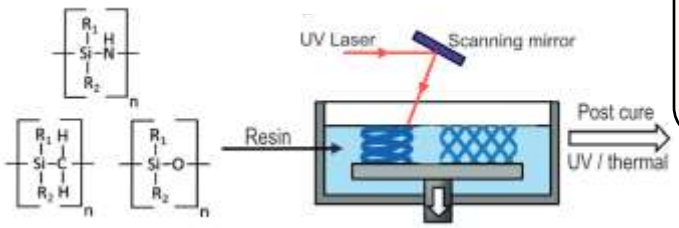
Oxidation of VOCs

Adsorbents

1. Ackley, B. J. et al. *Chem. Rev.* **2023**, 123, 8, 4188.
2. Colombo, P. et al. *J. Am. Ceram. Soc.* **2010**, 93, 1805.
3. Wang, H. et al. *Chem. Rev.* **2020**, 120, 9363.

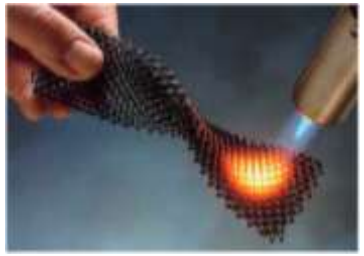
Structuration of polymer-derived inorganic materials

Macro-scale ordering

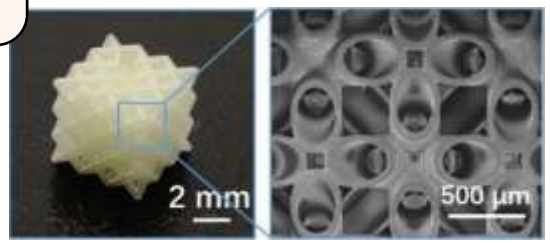


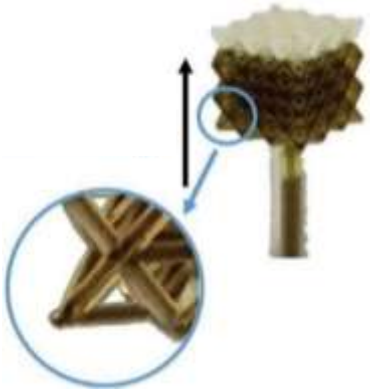
✖ *Access to ultra-small features*
✖ *Control over nanostructuration*
✓ *Complex geometries*

Science **2016**, 351, 58

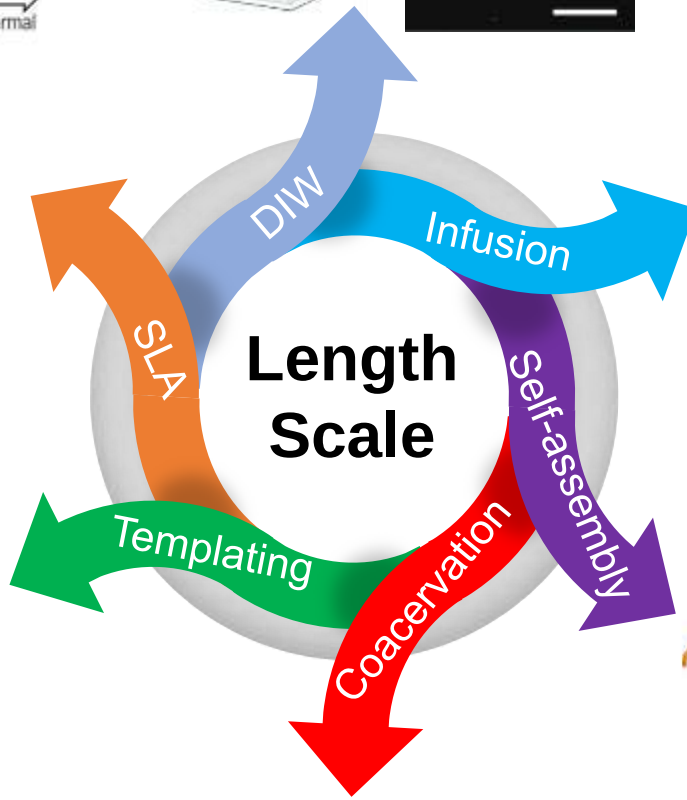


Adv. Mater. **2023**, 35, 2209270

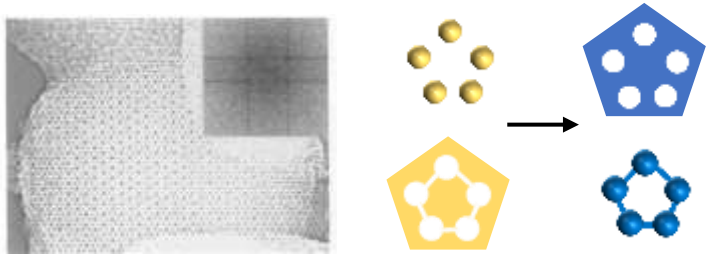




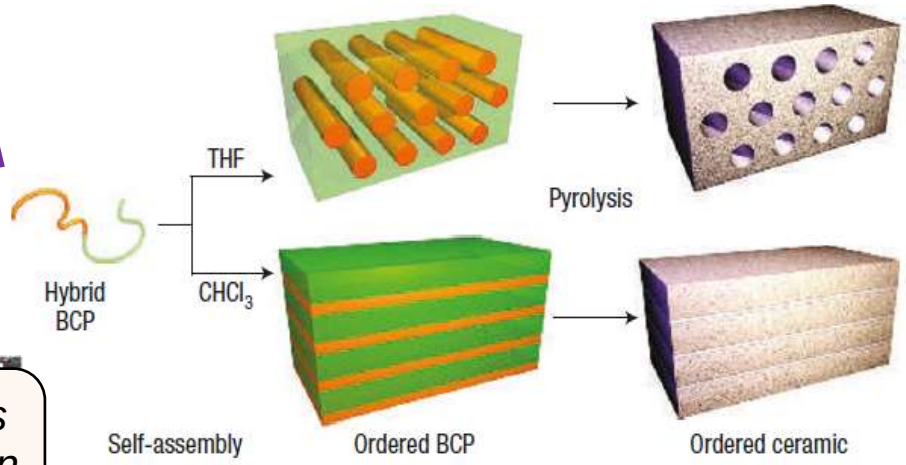
Adv. Funct. Mater. **2022**, 32, 2105879



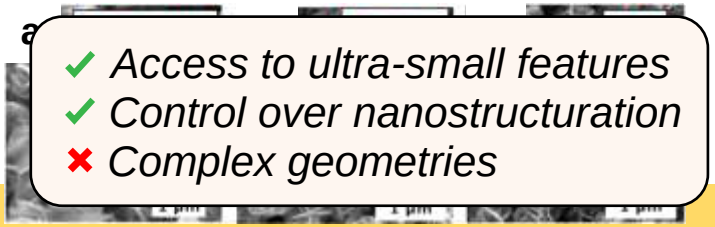
Nano-scale ordering



Science **1993**, 261, 1299



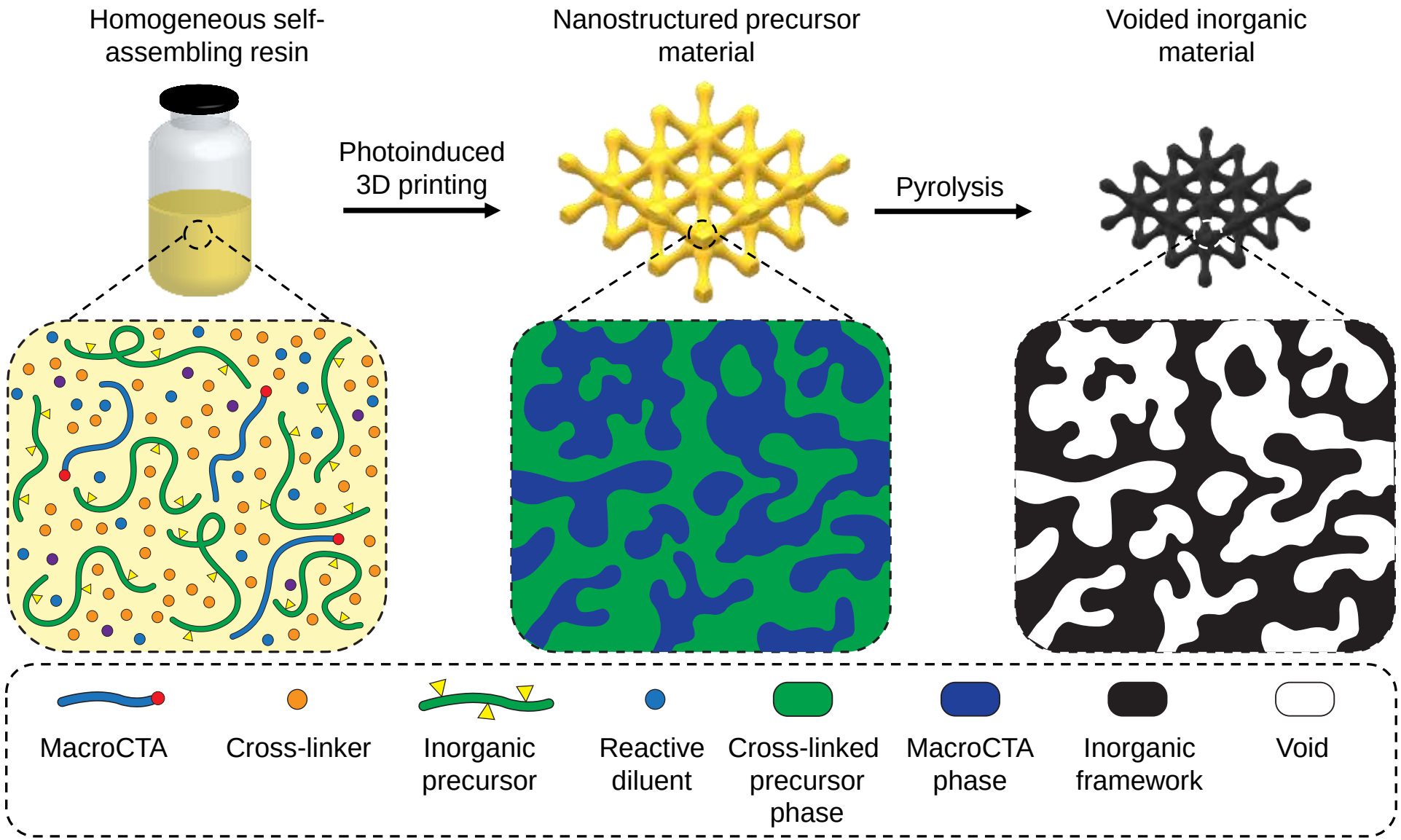
Nat. Nanotechnol. **2007**, 2 (1), 43



✓ *Access to ultra-small features*
✓ *Control over nanostructuration*
✖ *Complex geometries*

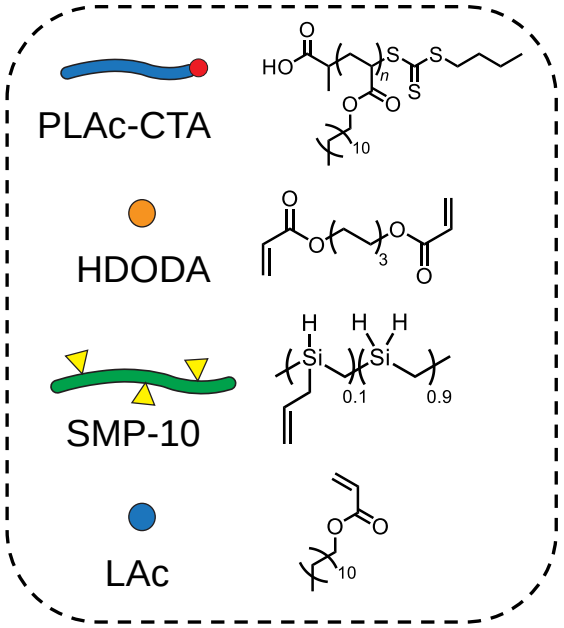
J. Am. Chem. Soc. **2018**, 140, 10297−10304

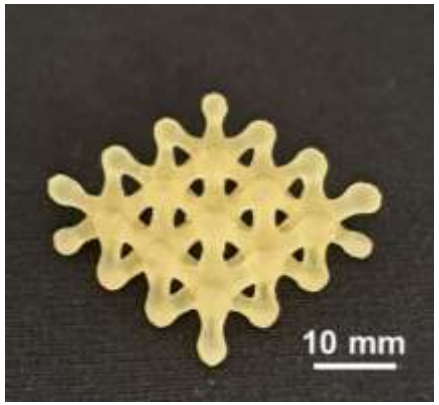
General route to 3D printed nanostructured inorganic materials



Customised nanostructured ceramics

Preceramic material



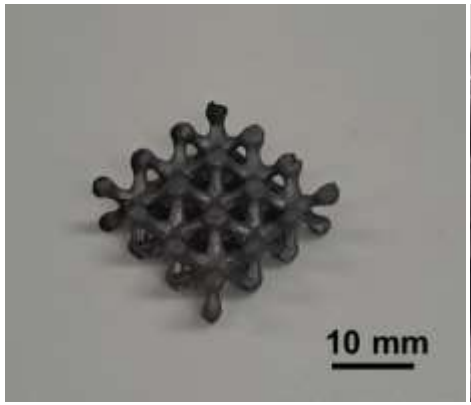


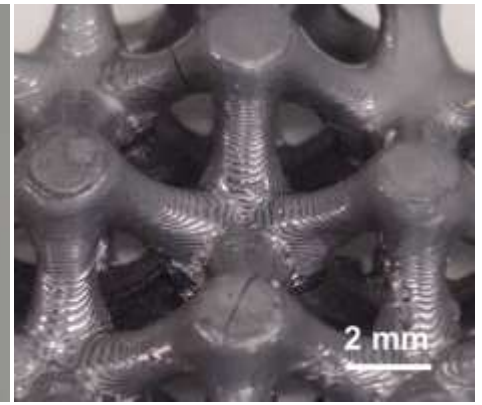
Pyrolysis

800 – 1200 °C
Argon

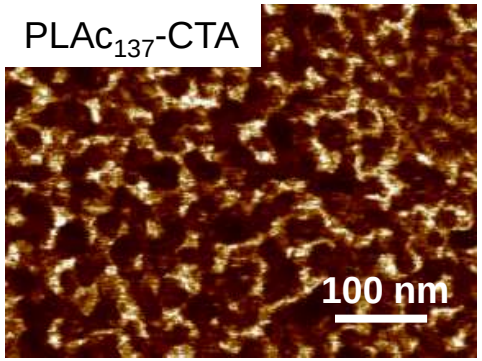
Isotropic
shrinkage ~ 30%

Nanoporous silicon oxycarbide (SiOC) ceramics

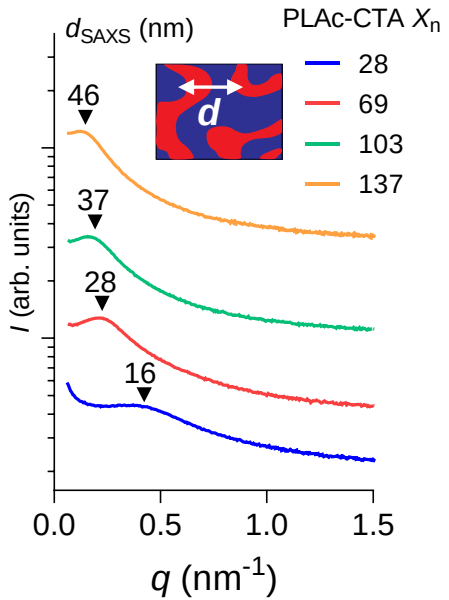




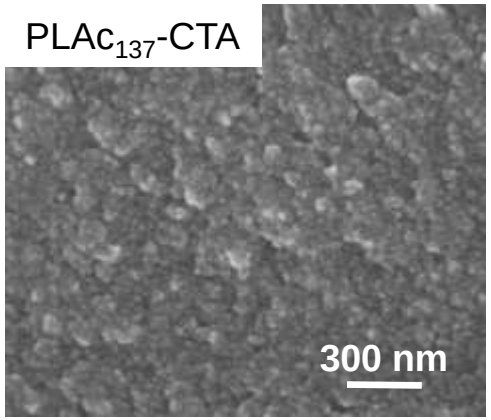
PLAc$_{137}$-CTA



0 MPa 650



PLAc$_{137}$-CTA



X_n of PLAc block	Surface area, m^2 g^{-1}	Pore connectivity (η), %
28	164	25
69	278	43
103	589	93
137	260	45

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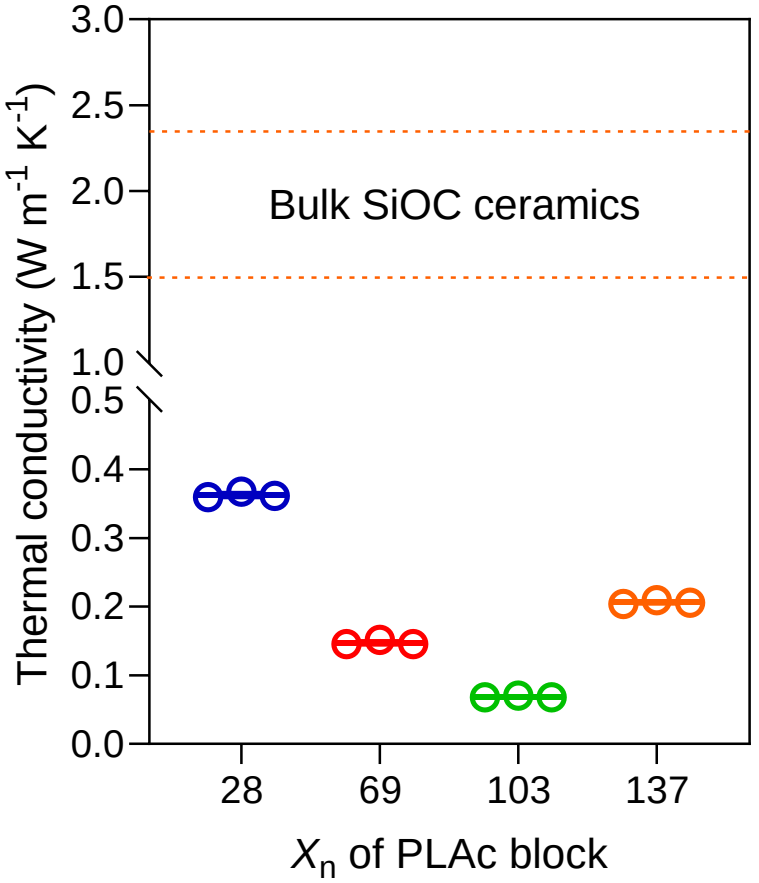
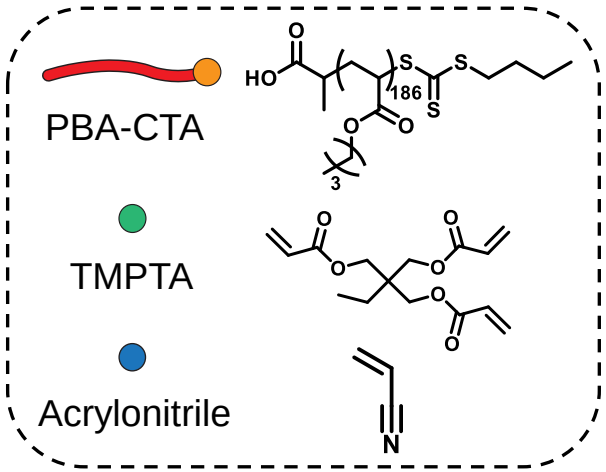
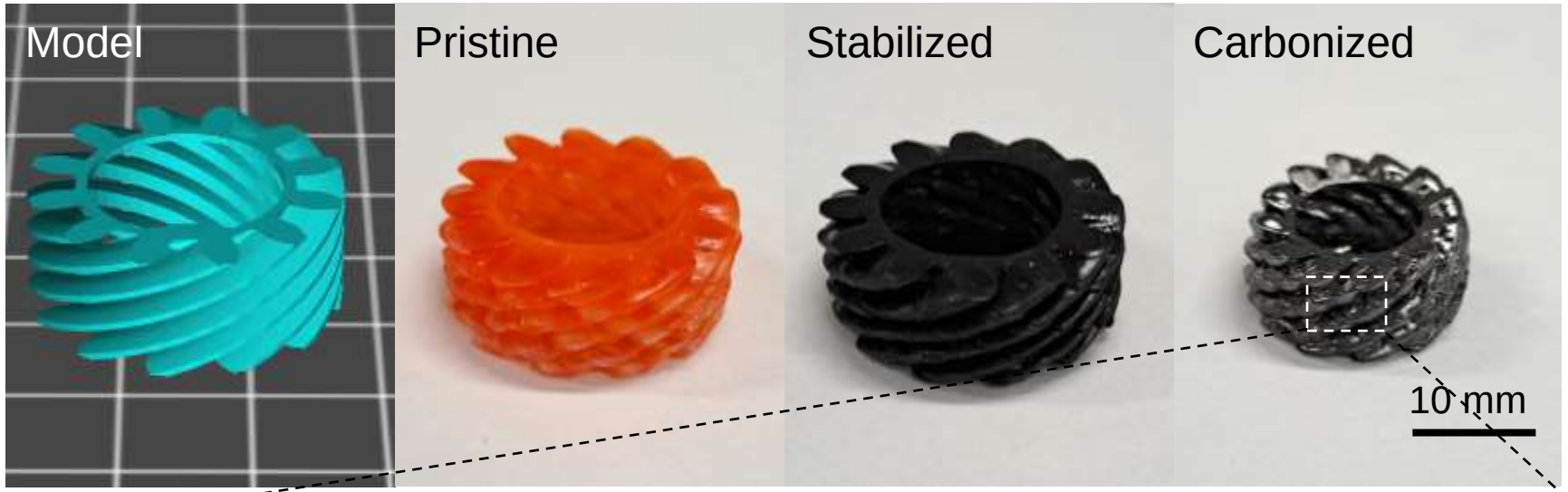
Thermal properties of PIMS ceramics

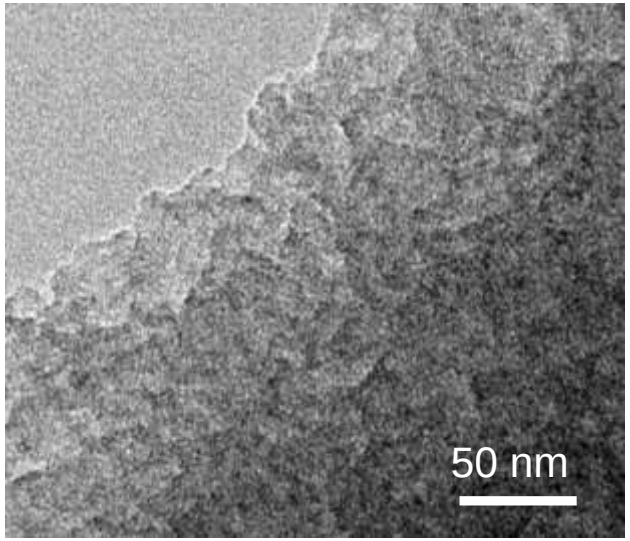
(speed up x4)

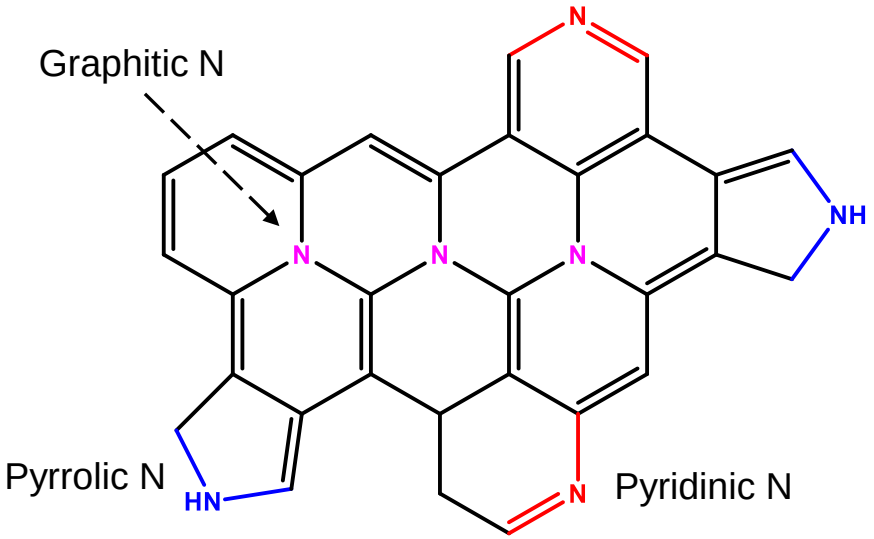


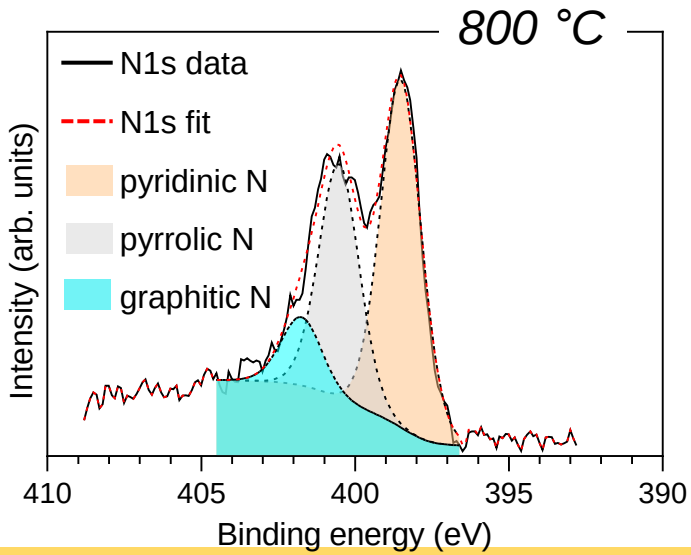
3D Printed nanostructured N-doped carbon







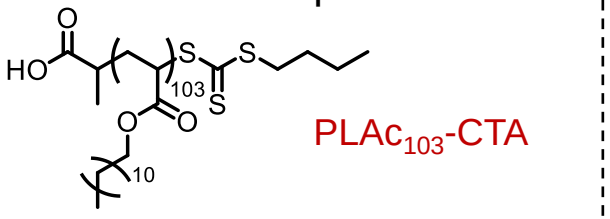




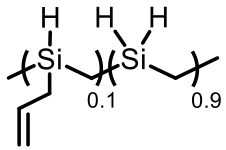
Bobrin, V. A., Hackbarth, H. G., Yao, Y., Kundu, D., Bedford, N. M., Kuchel, R. P., Zhang, J., Corrigan, N., Boyer, C. Design and 3D Printing of Polyacrylonitrile-Derived Nanostructured Carbon Architectures. Accepted. *Small Science*, **2024**.

3D Printing of carbon-ceramic composites

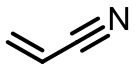
Core components



$PLAc_{103}$-CTA

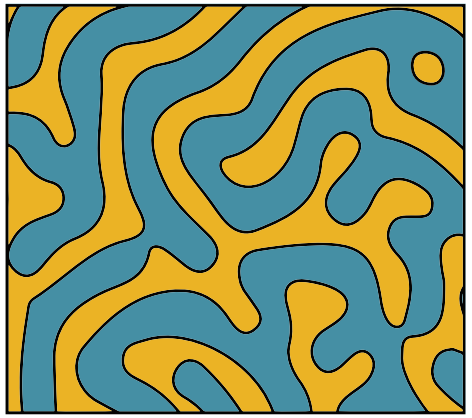


Preceramic precursor SMP-10



Carbon precursor AN

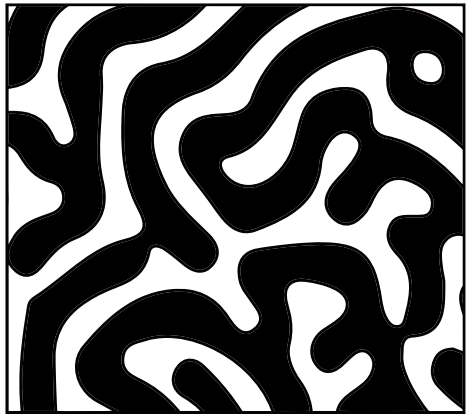
3D Printing



net-P(SMP-10-*co*-AN)

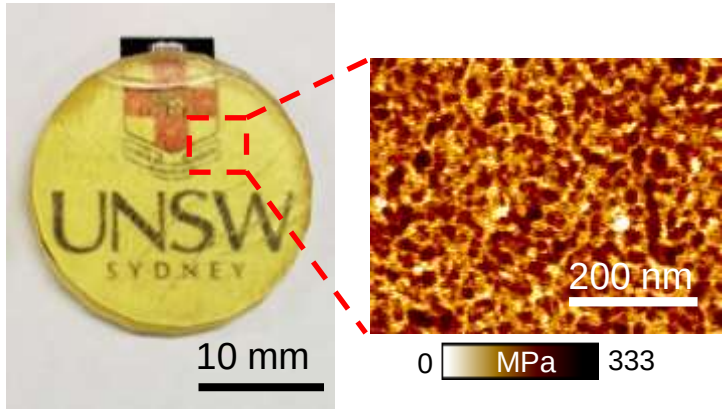
Sacrificial PLAc

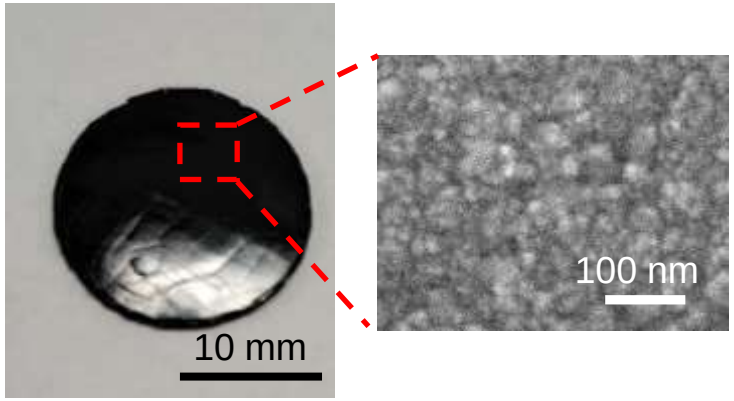
Pyrolysis



Carbon-ceramic matrix

Nanoscale voids





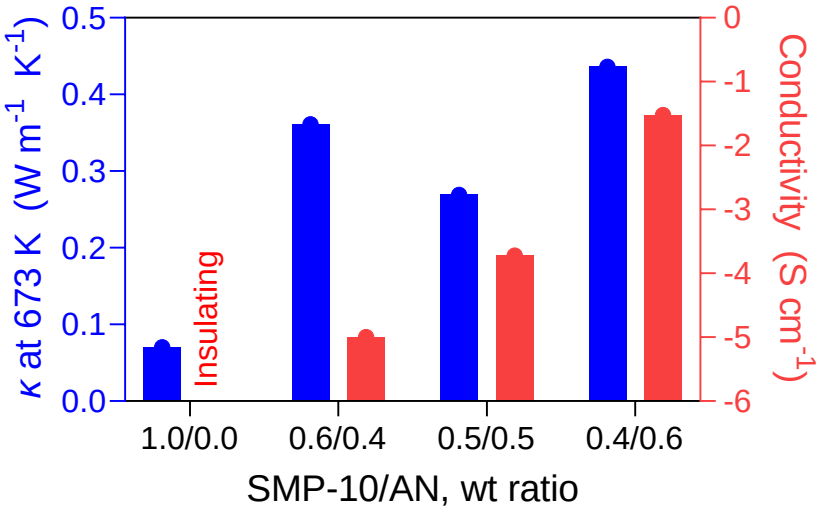
Manuscript in preparation.

Properties of 3D printed of carbon-ceramic composites

Carbon property

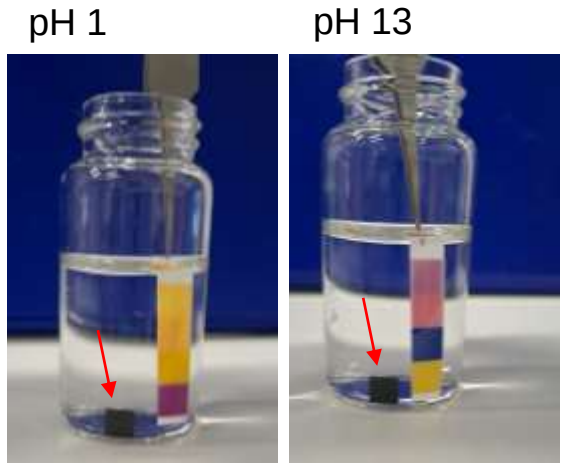
Ceramic property

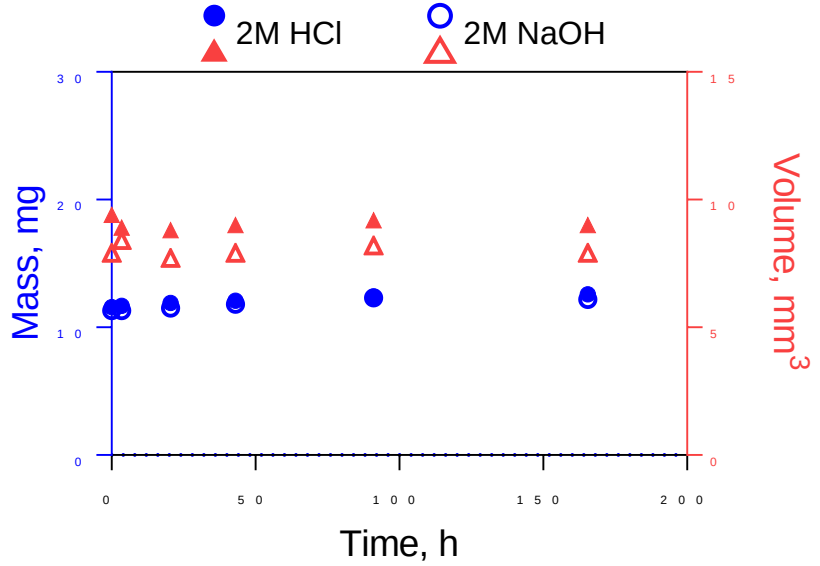
Thermal & electrical conductivity



Chemical stability

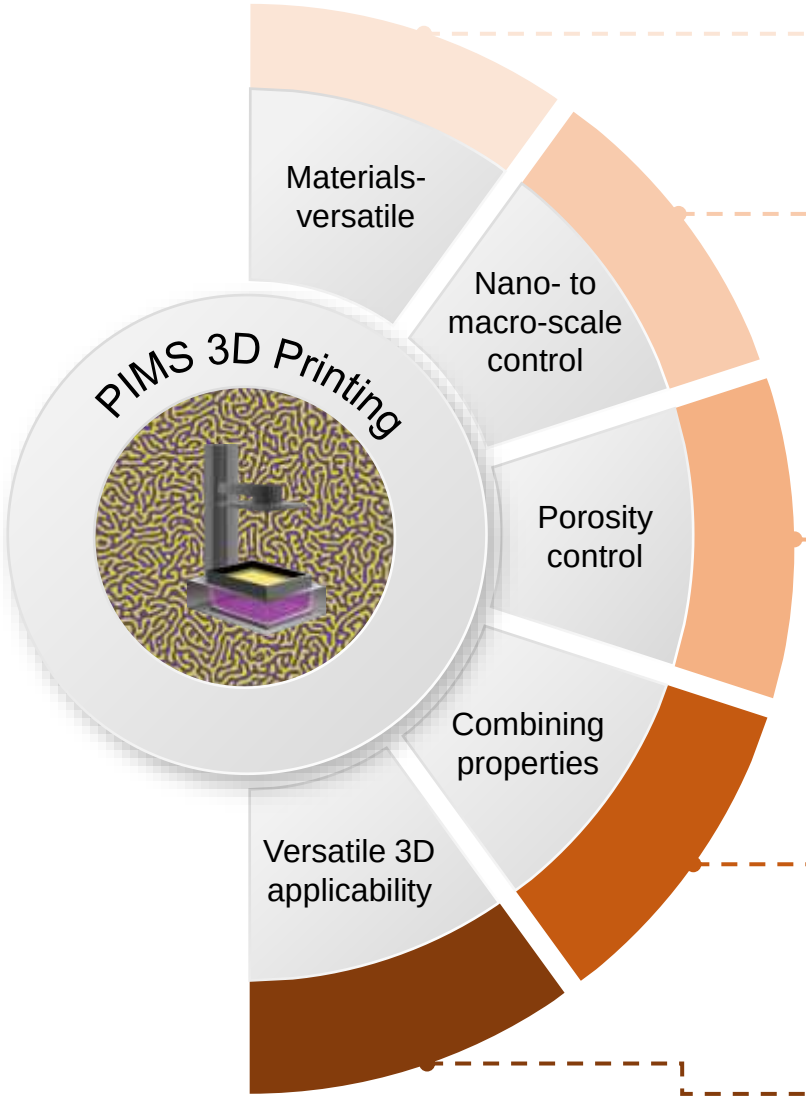
After 1 week

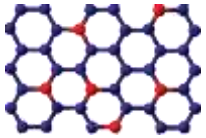




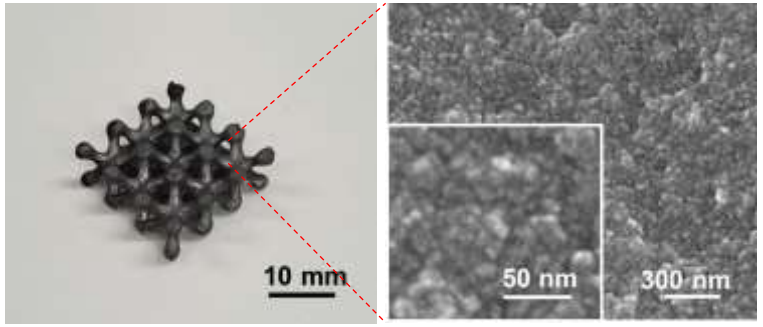
Manuscript in preparation.

Summary – features of our approach

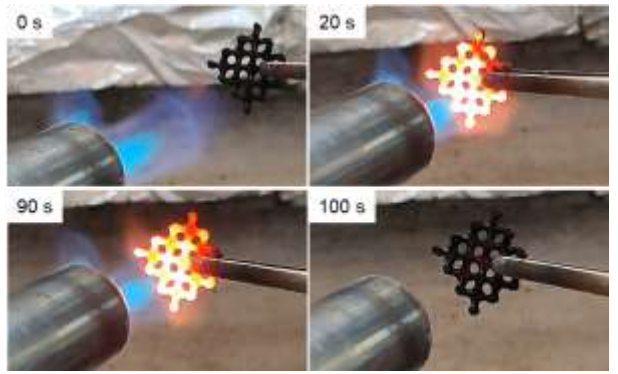


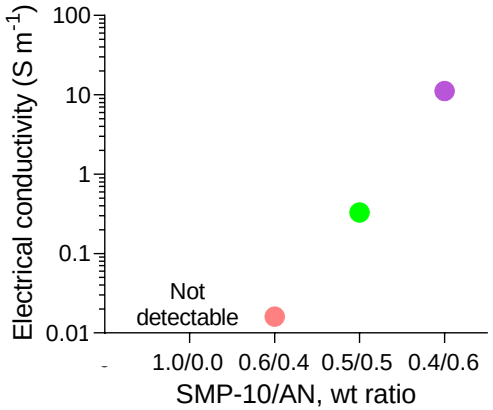


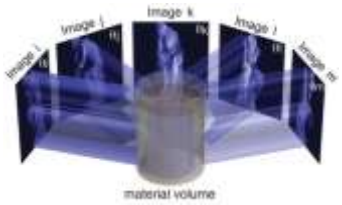
N-doped C

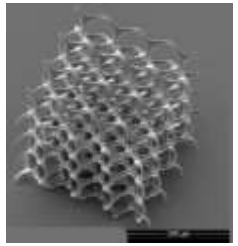


X_n of PLAc	Surface area, $m^2\ g^{-1}$	Pore volume (V_{pore}), cm^3
28	164	0.06
69	278	0.12
103	589	0.24









~ 400 AUD

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Questions?

Customised Nanostructured Inorganic Materials via Microphase Separation 3D Printing

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