PHOTOCURABLE SOL-GEL FORMULATIONS FOR ADDITIVE MANUFACTURING OF CERAMICS

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X Workshop Italiano Sol-Gel - Wednesday, September 16th, 2025 h 11.50

Additive manufacturing of ceramics: challenges

Conventional powder-based approaches

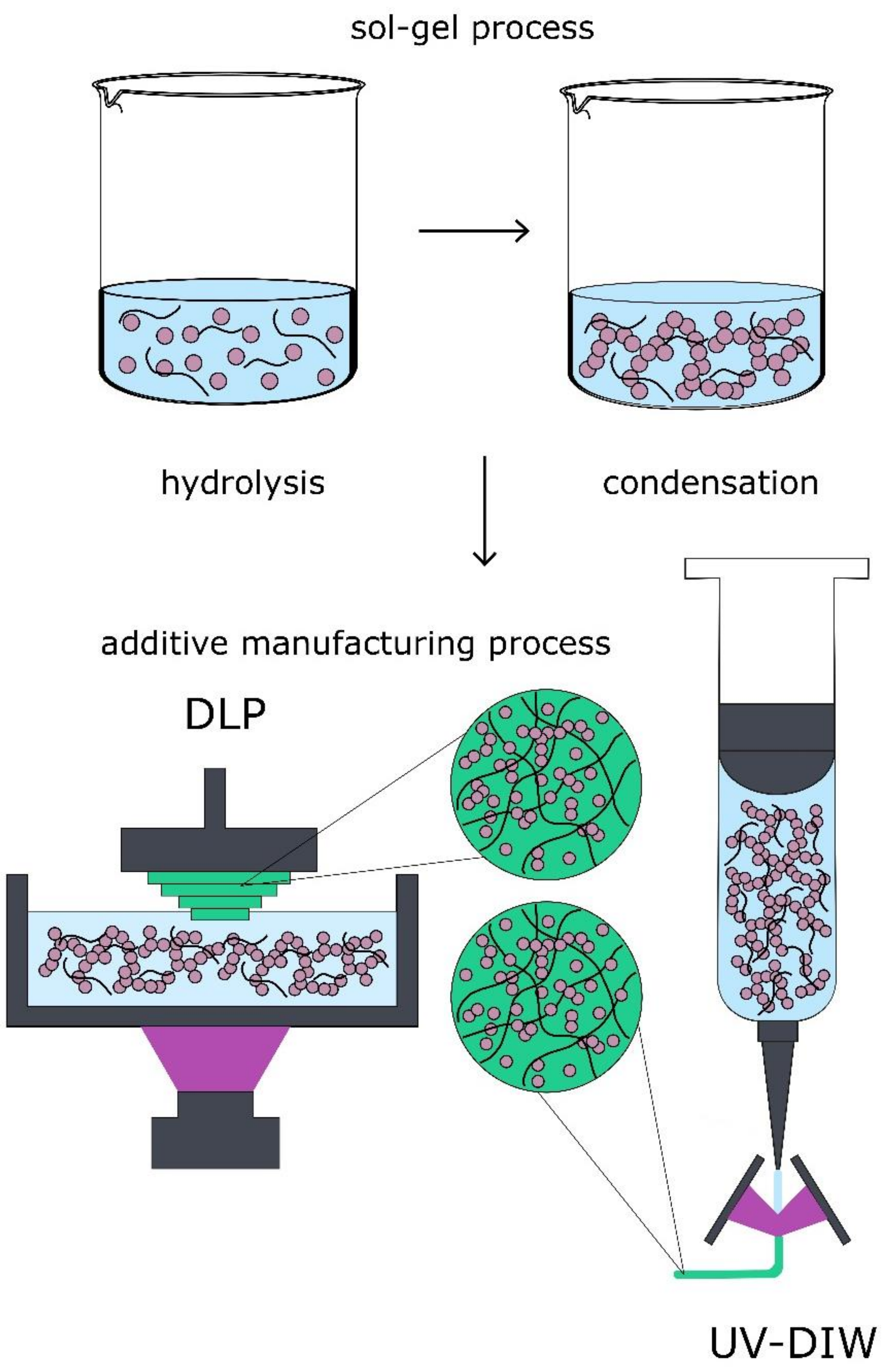
- fine ceramic powders to be dispersed in aqueous and non-aqueous slurries
  - high viscosity even with a limited amount of powder (~40%$_{vol}$)
- green bodies with adequate strength
  - significant amount of organic binders
    - delicate debinding processes and limited wall thickness and volume
- particle size limits the resolution, feature size and surface quality
- light scattering limits the resolution and penetration depth (DLP, SLA)

Liquid feedstock

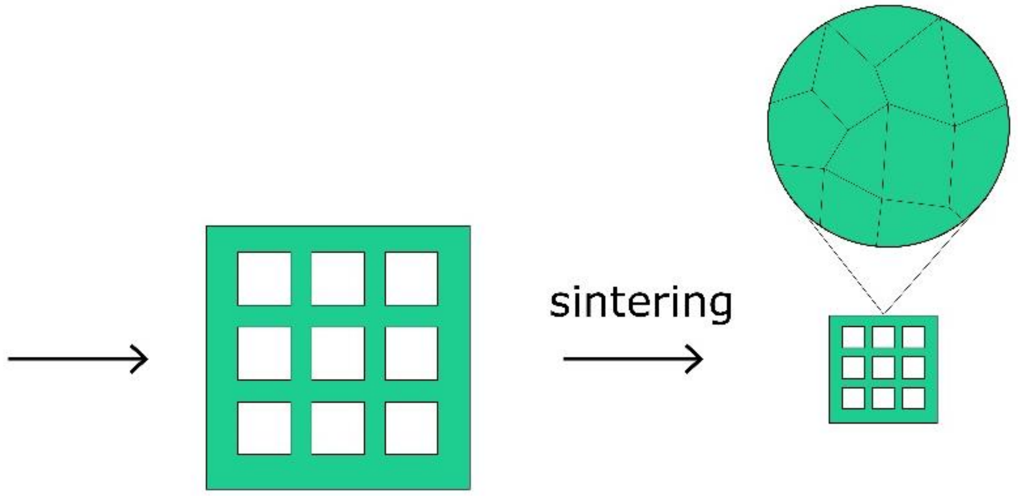
- liquid systems exploit the more advanced stage of development of AM technologies for polymers
- densification occurs at lower temperatures and generally results in denser bodies
  - stronger and more reliable parts
  - unique maaaaaterial properties retained (i.e. glass transparency)
- not suitable for all AM technologies (~~BJ~~, ~~SLS/SLM~~, ~~DED~~)

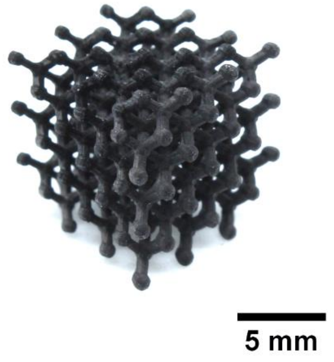
G. Franchin et al., CJME:AMF, 1 (2022) 100012

Sol-gel compositions for AM processes

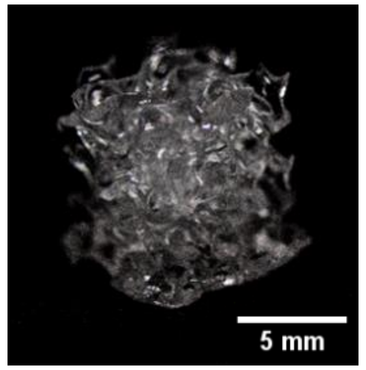


- chemical versatility
- high homogeneity of the final product
- material design by assembling molecular building blocks
- fine tuning of the material properties
- preventing clogging of the tip during extrusion-based processes
- control on reactivity by tailoring synthesis parameters: temperature, pH, catalyst system, precursor:solvent ratio





TiC/C

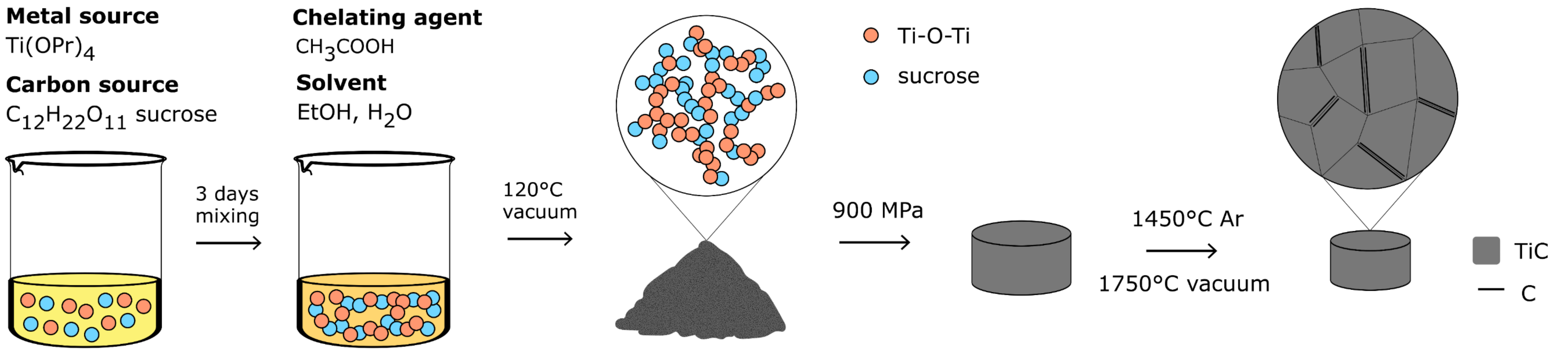


multicomponent glass

DLP of hierarchically porous carbide/carbon nanocomposite

- *note:* carbide powder-based suspensions produce light adsorption and scattering
  → hindered photopolymerization and penetration depth
- *application*: targets for isotope on-line separation (ISOL) facilities
  → nuclear physics and radiopharmaceutical applications

Highly microporous TiC/C nanocomposite



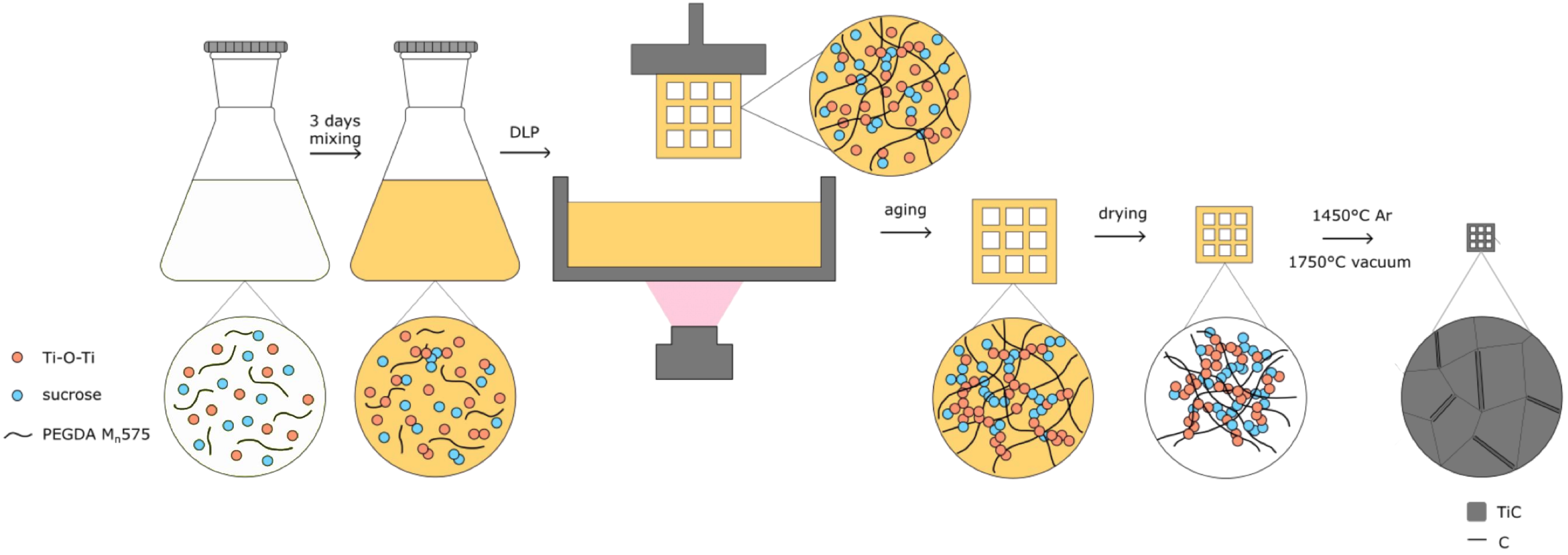
- metal and carbon precursors + carbothermal reduction → highly porous carbide
- overstoichiometric carbon content: $TiO_2 + 5C \rightarrow TiC + 2C + 2CO$

  → excess C = turbostratic structure

  → thin sheets at the grain boundaries of TiC nanocrystals (22 nm)
- total porosity: 64% (97% of which open)
- SSA (BET): 655 m^2/g, micropores fraction: 84%

Zanini A. et al., Microporous and Mesoporous Materials 2022, 337, 111917

Photocurable ink for AM of TiC/C nanocomposite

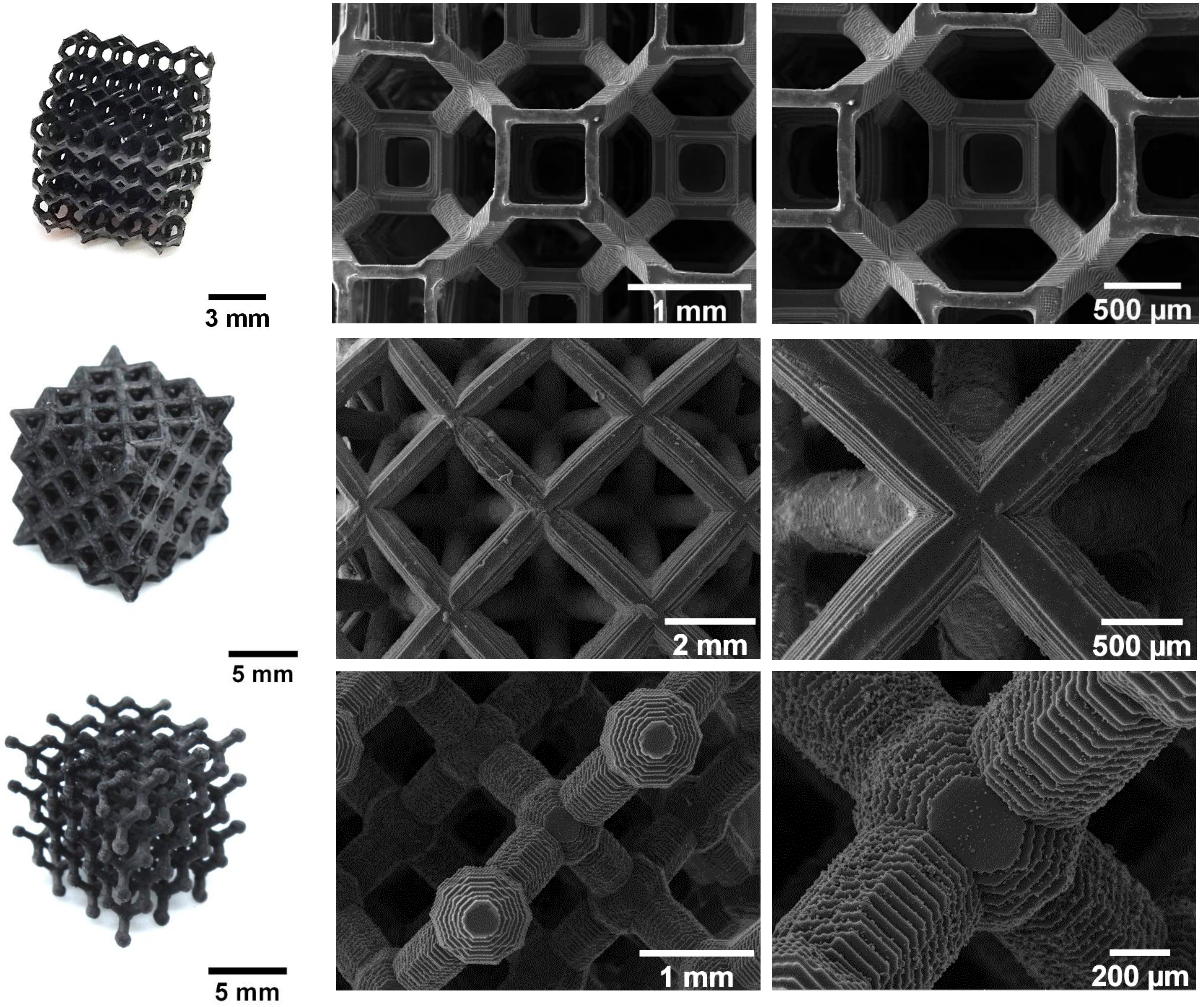


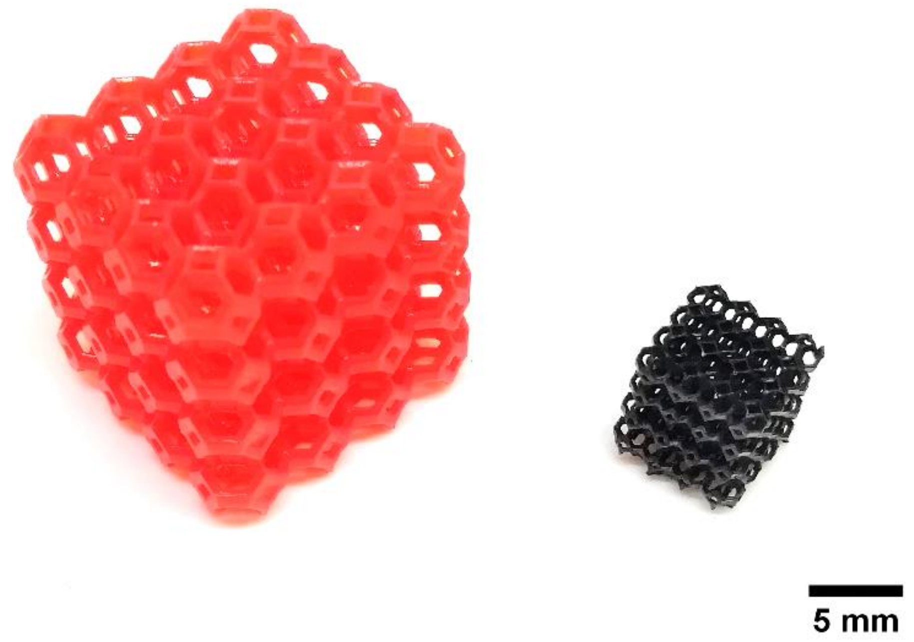
→ physical blend of the sol and a photocurable acrylate (PEGDA) to promote fixation by photopolymerization reactions

→ formation of 2 separate, interpenetrating networks (sol-gel and photopolymerization-derived)

A. Zanini et.al., ACS Appl. Mater. Interfaces 16, 51 (2024) 70828–70838

DLP of structured hierarchically porous TiC/C nanocomposite





- crack-free samples upon sintering at 1750°C
- dense struts and no residual porosity
- homogeneous shrinkage along x-y and z direction

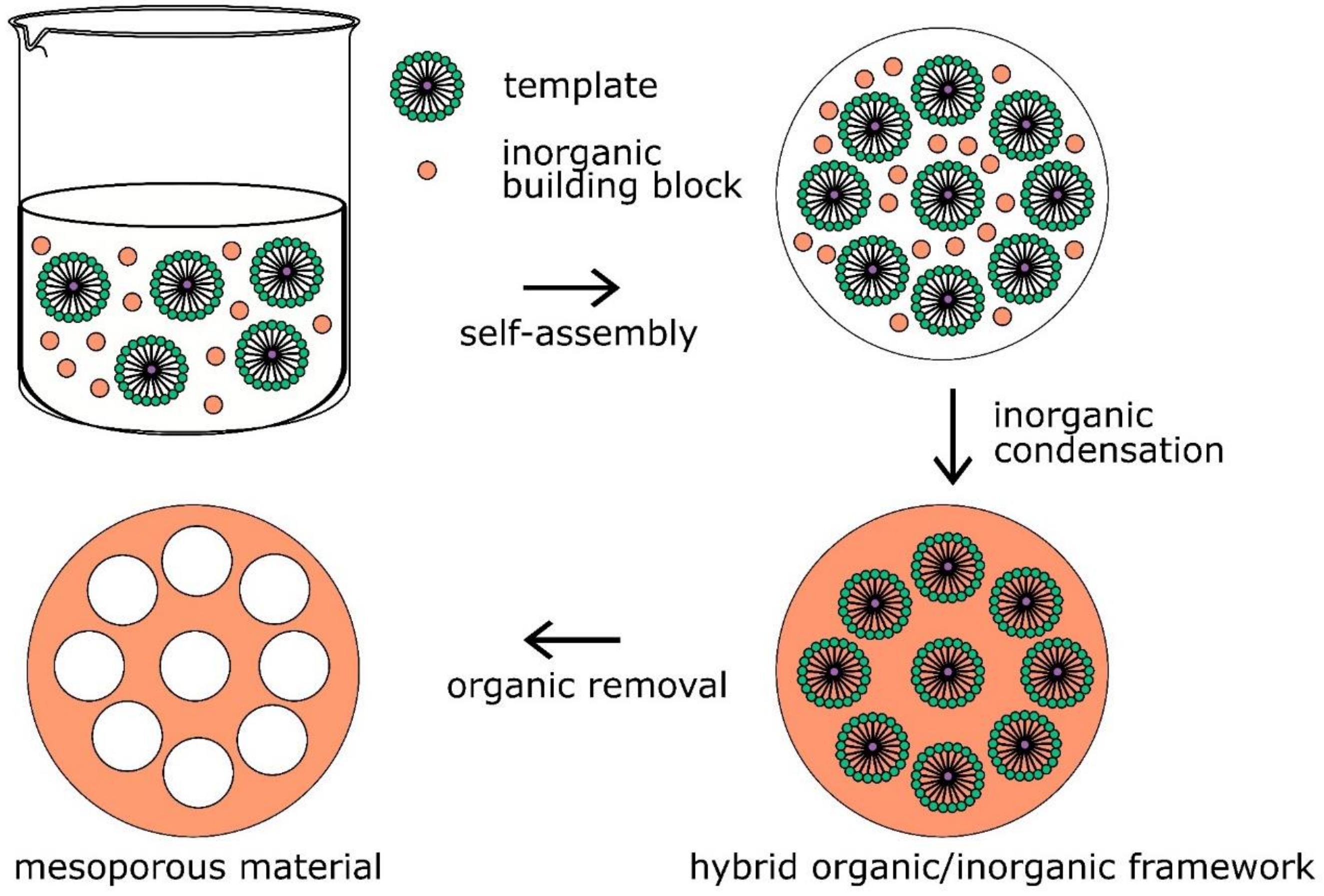
weight loss [%]	91.1 ± 0.7
xy shrinkage [%]	56.7 ± 0.1
z shrinkage [%]	56.7 ± 0.1
volumetric shrinkage [%]	91.9 ± 0.1

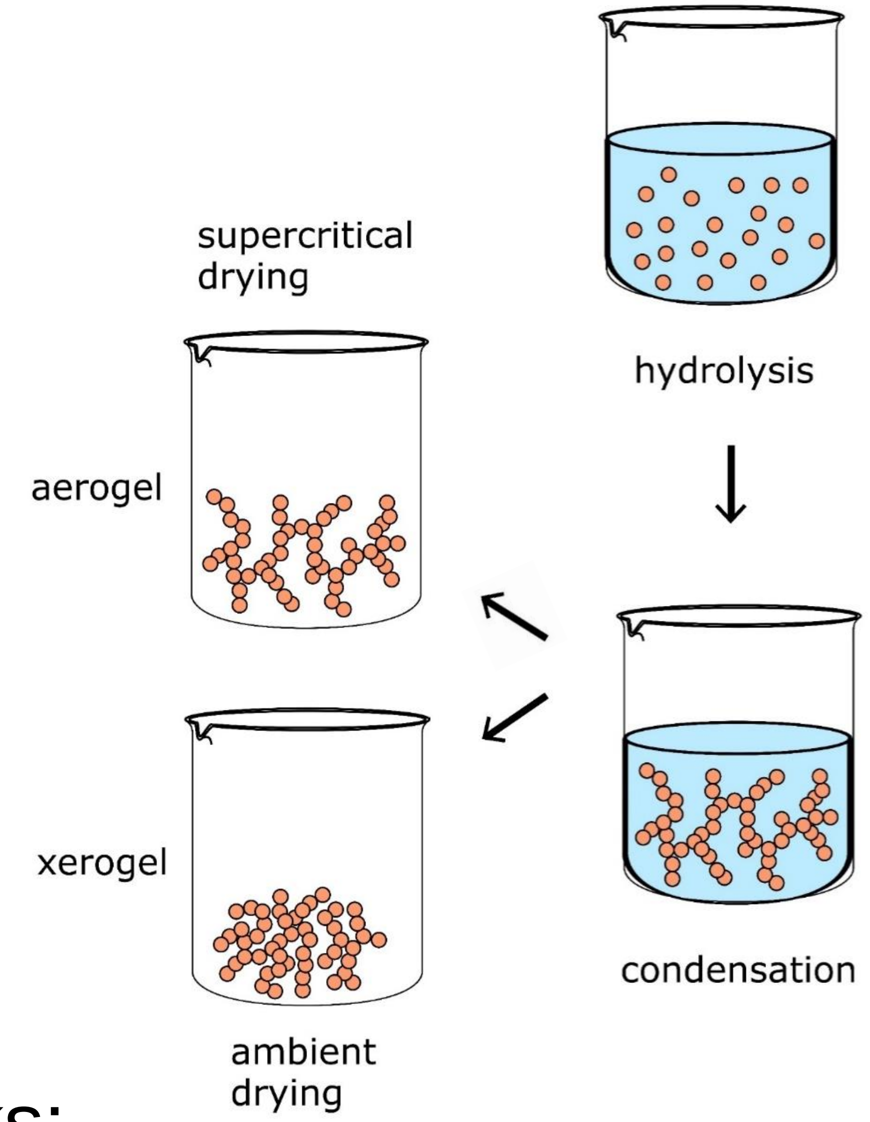
A. Zanini et.al., ACS Appl. Mater. Interfaces 16, 51 (2024) 70828–70838

DLP of structured hierarchically porous TiC/C nanocomposite

- volumetric shrinkage of photopolymer upon photopolymerization

  → textural changes in the final material SSA (BET): 149 m^2/g





→ control over the local arrangement of the molecular building blocks:

- EISA (evaporation induced self-assembly)
- supercritical drying
- cooperative EISA + supercritical drying

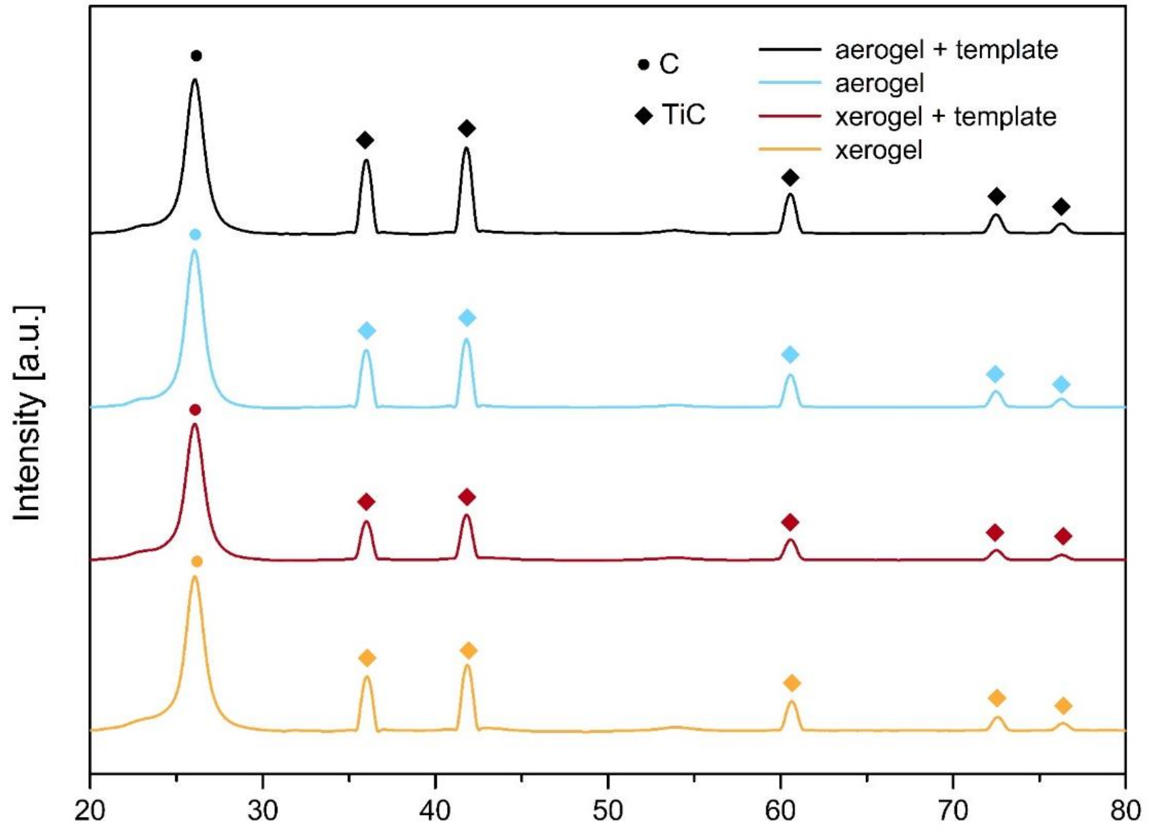
A. Zanini et.al., *ACS Appl. Mater. Interfaces 16, 51 (2024) 70828–70838*

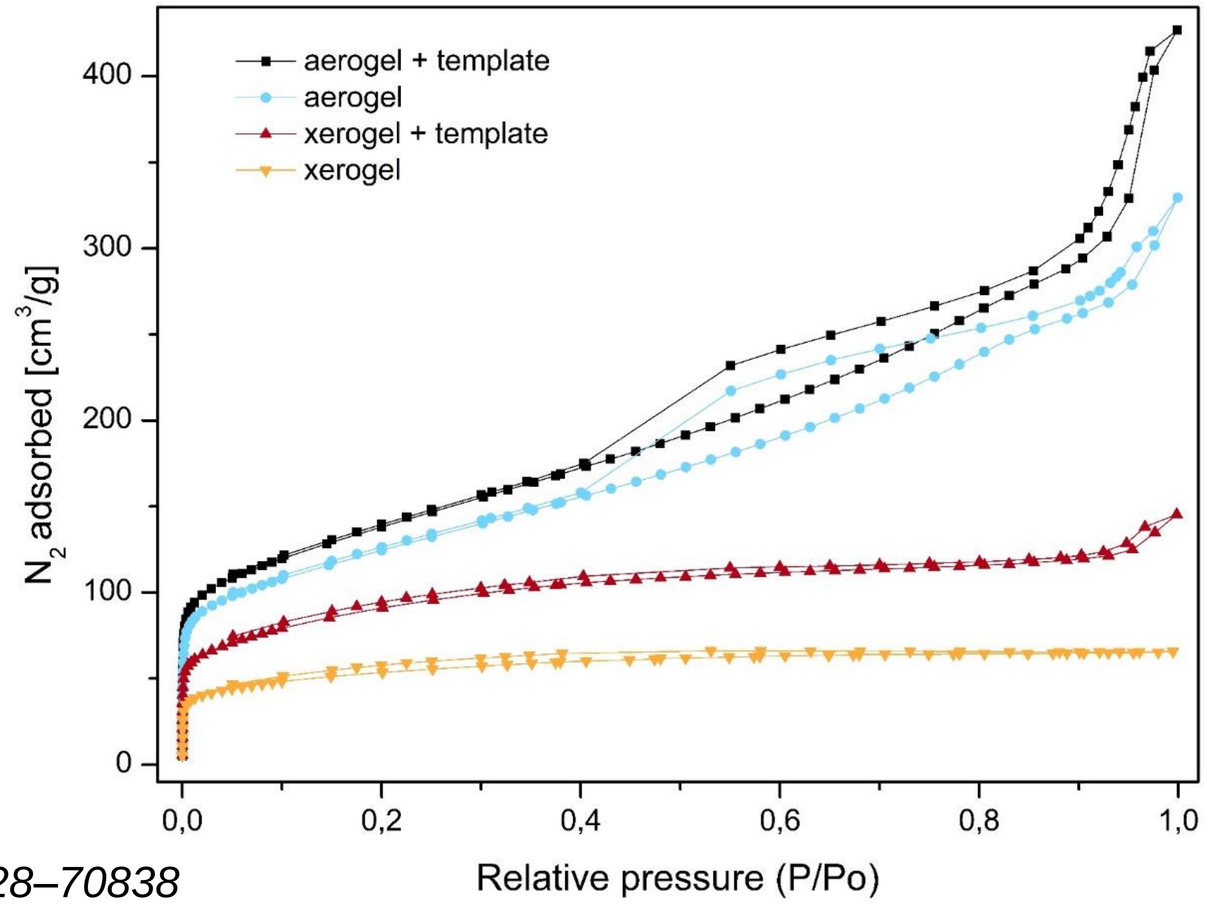
DLP of structured hierarchically porous TiC/C nanocomposite

- overstoichiometric carbon content: Ti : C = 1 : 5
  - → TiC nanocrystallites (13 nm)
  - → nanocrystalline graphite (7 nm) with turbostratic stucture

- textural control and design of bimodal porosity:
  - aerogel route → mesopores > micropores
  - xerogel route → mesopores < micropores

fabrication route	SSA_{BET} [cm^3/g]	V_{micro} [%]
xerogel	149	71
xerogel + EISA	328	57
aerogel	391	21
aerogel + EISA	403	18



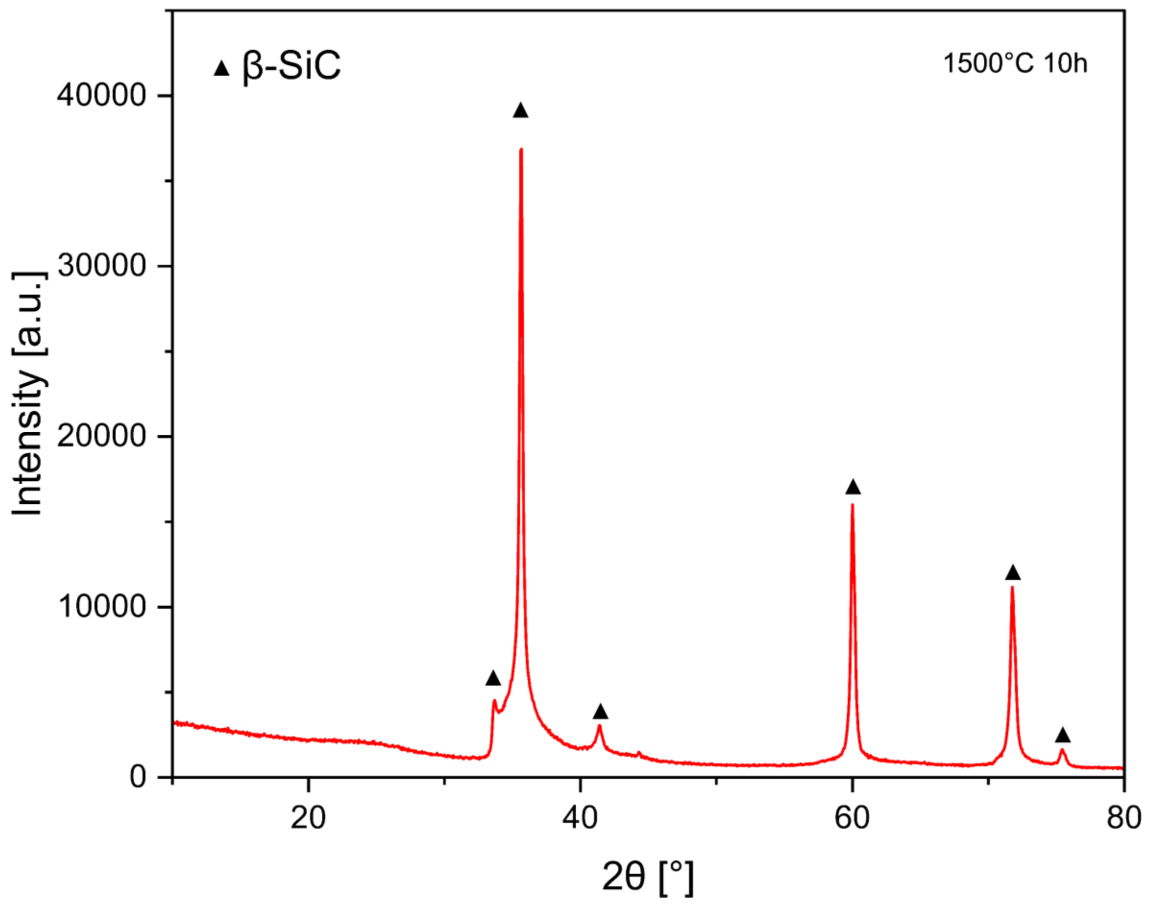


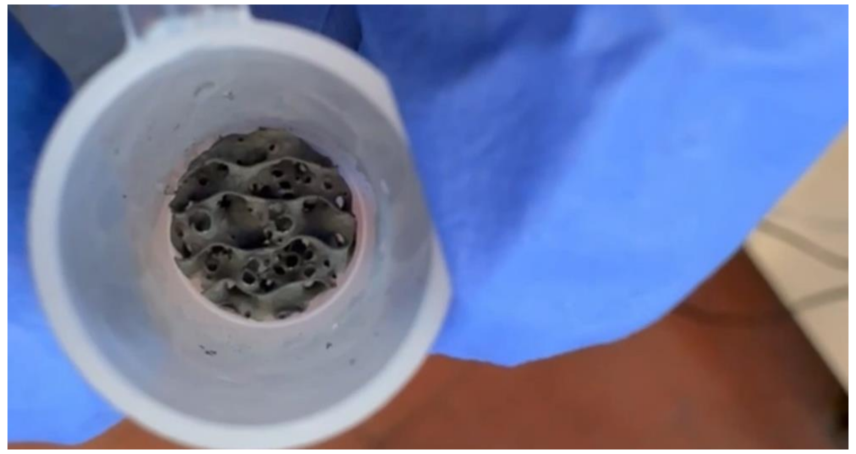
A. Zanini et.al., ACS Appl. Mater. Interfaces 16, 51 (2024) 70828–70838

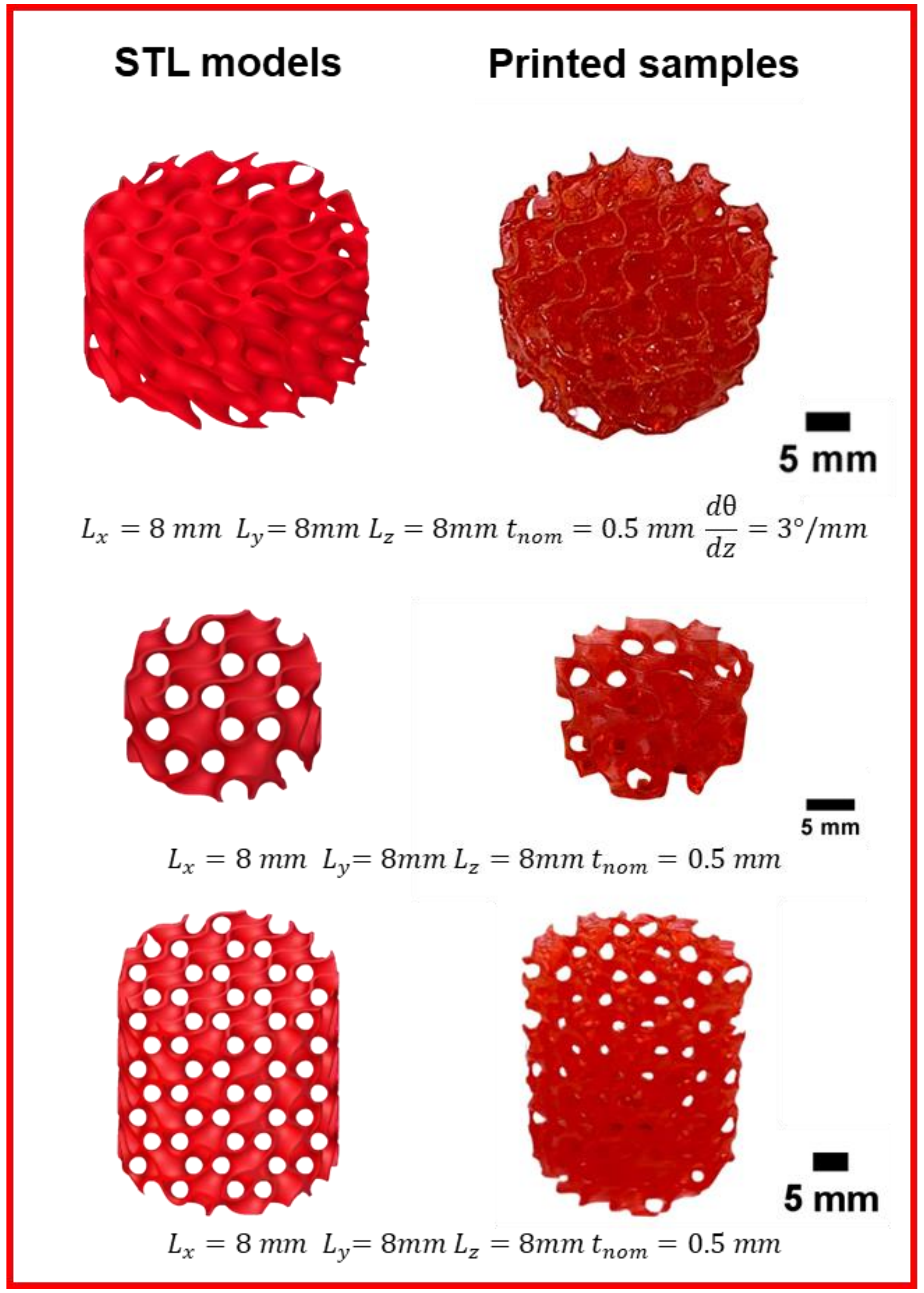
Current research: nanostructured SiC

- stoichiometric carbon content:
  Si : C = 1 : 1
  - → TEOS + sucrose (~ TiC)
  - → other hybrid Si-C precursors

- thermal treatment @ 1500°C for 10h in high vacuum







Precursors	SSA_{BET} [cm^3/g]	Crystallite size [nm]
TEOS + sucrose	42	27
other	372	26

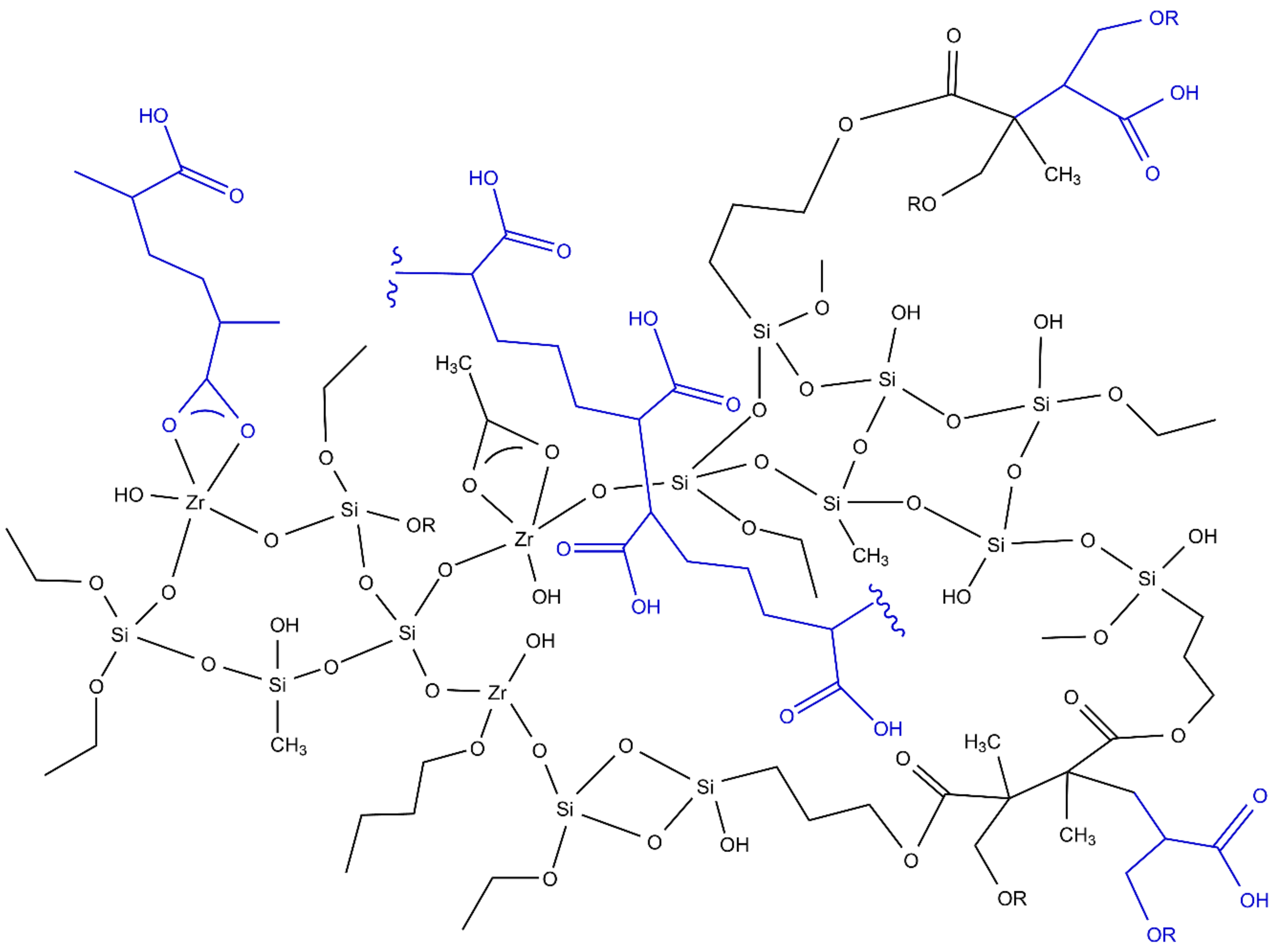
DLP and UV-DIW of dense multicomponent glass

- high transmittance
- compositional versatility

  → tuning of refractive index and other optical properties
- *application*: jewelry, optics

Photocurable sol-gel formulations for multicomponent glass

- **Si precursors**: alcoxides
  - *hydrolizable groups*: hydrolysis/condensation
  - *non-hydrolizable groups*: chain flexibility
  - ***acrylate groups***: photopolymerization (interconnected networks)
- **Transition metal precursors**: alcoxides
  - Zr, Ti to increase the refractive index
- **Non-hydrolizable acrylate monomer**: partial decoupling of the two networks to turn material rigidity and response to stresses
- **High boiling point solvent**: transient porosity to favor binder burnout



Patent pending (Swarovski) - PCT/EP2024/051082

A. Zanini et.al., Additive manufacturing of multicomponent glasses with enhanced optical properties via sol-gel, Additive Manufacturing 109 (2025), 104864

DLP of high refractive index glass

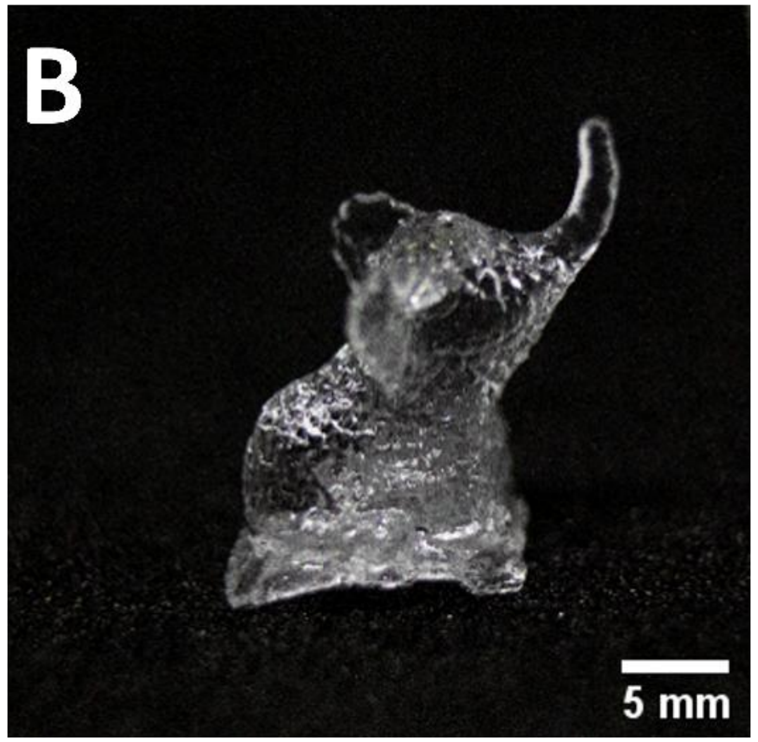
- precursors: SiO_2, ZrO_2 and TiO_2
- acid catalysis
- Si-alkoxide-acrylate + organic acrylate
- sintering T: 1000°C

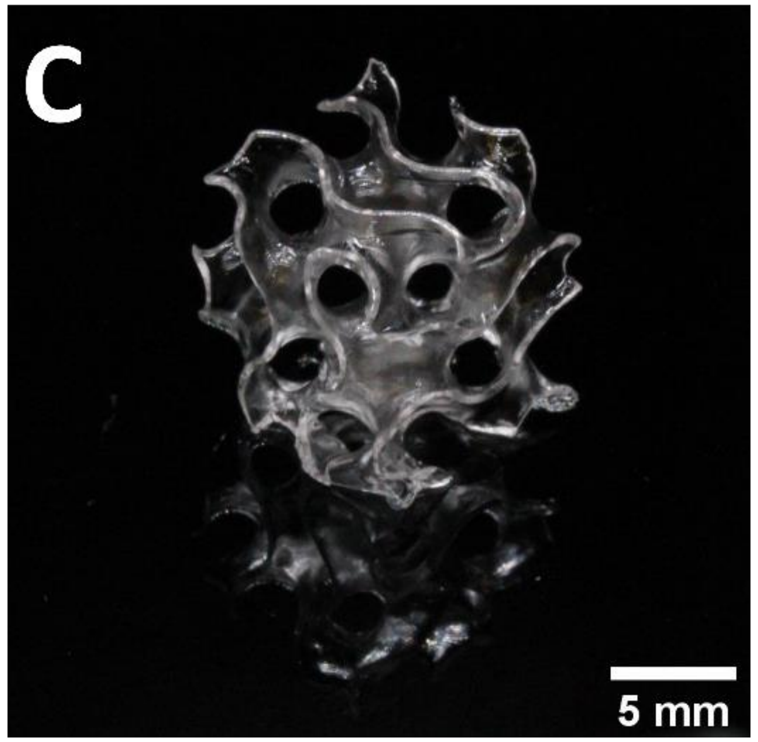
n_d: ~1.55 to ~1.57

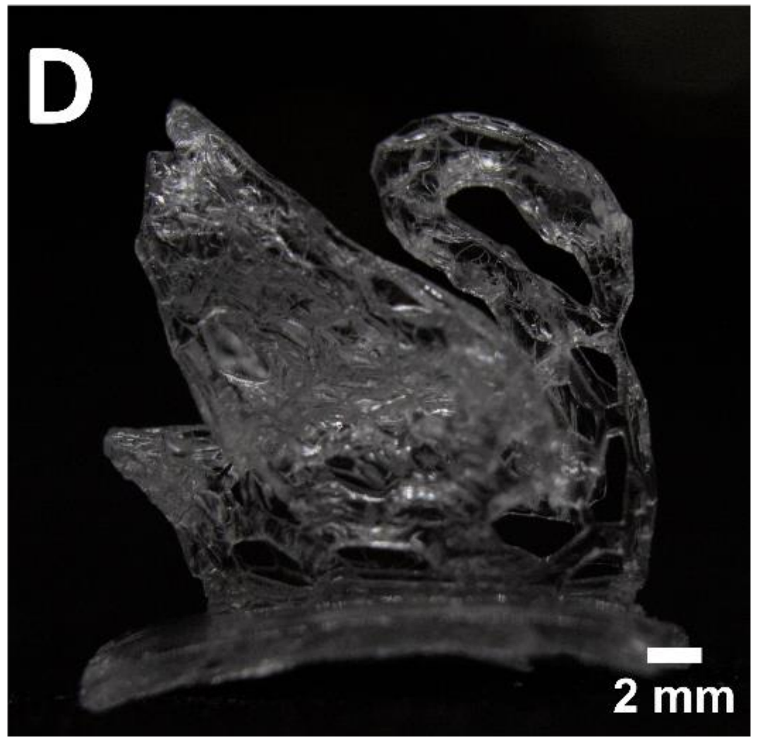
transmittance$_{@405\ nm}$: ~90.5 to 98.8%

density: ~2.55 to 2.72 g/cm^3

Abbe number: v_d ~41.3 to 60.4







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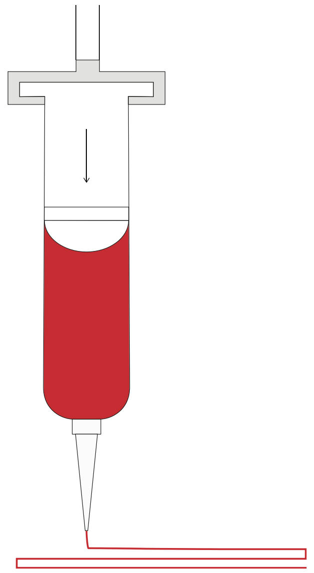
A. Zanini et.al., Additive manufacturing of multicomponent glasses with enhanced optical properties via sol-gel, Additive Manufacturing 109 (2025), 104864

Hybrid UV-DIW technology

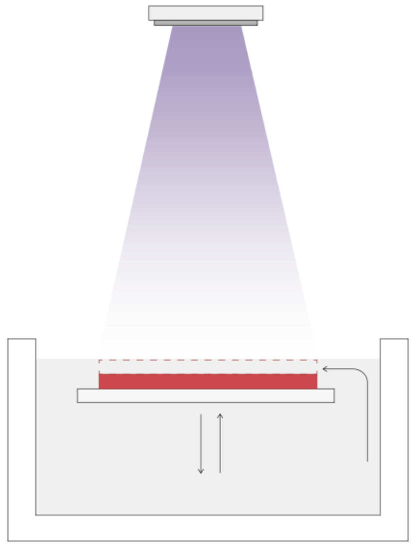
Hybrid additive manufacturing technology as a combination between Direct-Ink Writing (DIW) and UV photo-polymerization

Direct Ink Writing

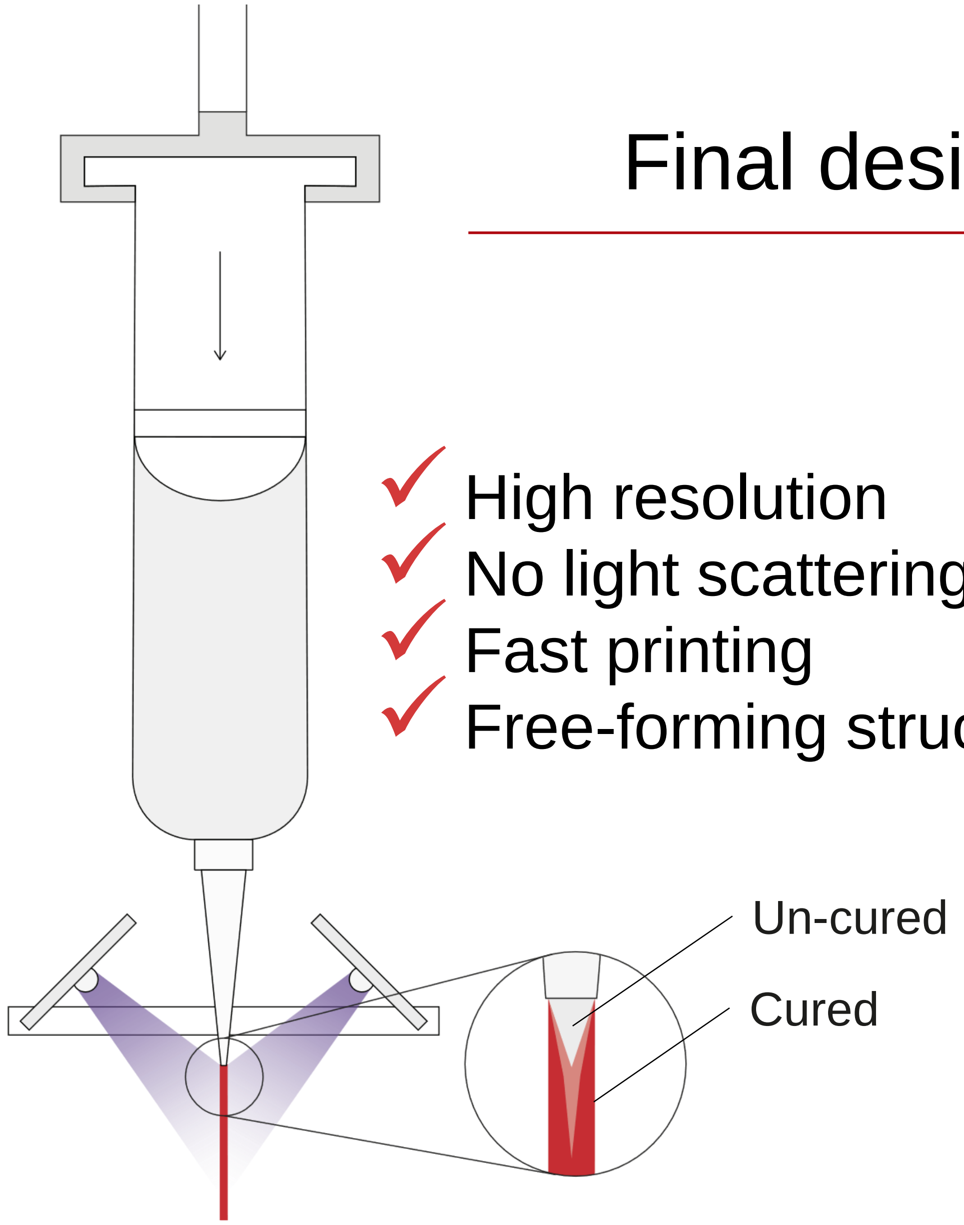


- ✓ Fast printing
- X Ink preparation

Vat photo-polymerization



- ✓ High resolution
- X Light scattering

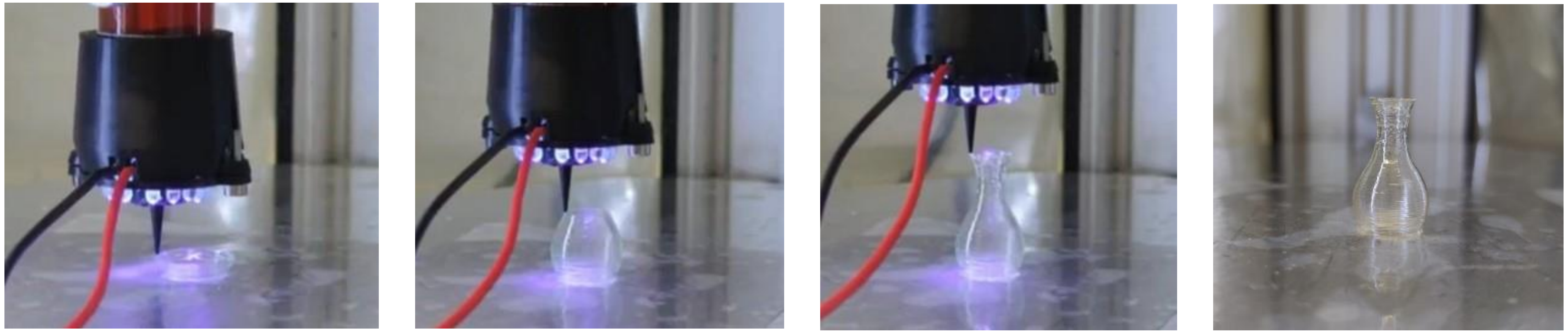


Final design

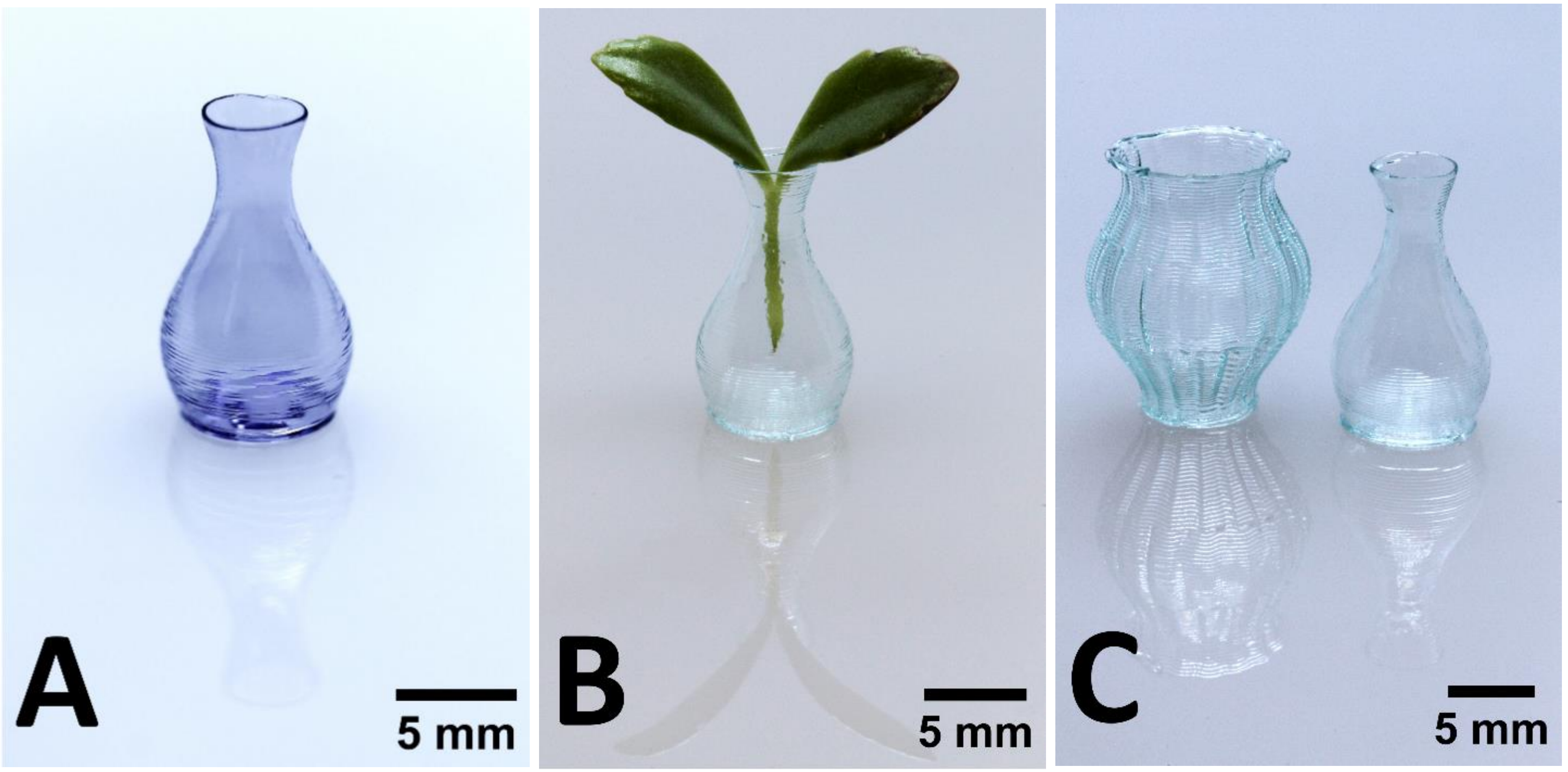
- ✓ High resolution
- ✓ No light scattering
- ✓ Fast printing
- ✓ Free-forming structures

A. De Marzi et al., Additive Manufacturing 54 (2022), 102727.

UV-DIW of high refractive index glass



- precursors: SiO_2, ZrO_2 and TiO_2
- acid catalysis
- Si-alkoxide-acrylate
- *addition of bulk coloring pigments*
- solvent evaporation step: tune ink viscosity
- sintering T: 1000°C
  → colored glass



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Summary and conclusions

- AM of sol-gel compositions demonstrates the potential of **liquid feedstock** for a facile production of porous and dense ceramic components:
  - sols can be rendered photocurable and exploited for **DLP** as well as other photopolymerization-based AM technologies
  - gel formation develops rheological properties suitable for **DIW**

    → hybrid **UV-DIW** technology
  - generation of two co-continuous networks (which can be separate or interconnected):

    → one organic (based on photopolymerized acrylates)

    → one inorganic (based on condensed M-OH groups from hydrolyzed metal alkoxides)
  - composition design to control solvent evaporation, reactivity, printing, drying, debinding and sintering

\+ high **versatility** in terms of composition and microstructural development

\+ structures with **controlled** (non stochastic) and **hierarchical** architectures

G. Franchin et al., CJME:AMF, 1 (2022) 100012

CERAMGLASS

advanced ceramics and glass research group

https://research.dii.unipd.it/ceramglass/

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