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Top-down control of bottom-up material synthesis @ nanoscale

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3D solidification of photo-polymerisable mixtures using ultra-short laser pulses can open new directions in formation of glass-ceramics with resolution at tens-of-nanometers.

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In a recently published paper in *Opto-Electronic Advances*, Mangirdas Malinauskas and his colleagues at Vilnius University report on a new high resolution inorganic material synthesis pathway using 3D laser printing and calcination. 3D metamaterials (beyond what exist in nature) emerge from research in high-resolution 3D polymerisation/printing where proportions of inorganic parts of a composit can be widely tuned[1]. By adding a high temperature annealing (HTA) post-fabrication step of sintering/calcination in air/oxygen flow[2–5] after the 3D polymerisation, a new glass and/or ceramic 3D structure with nanoscale features and large down-sizing can be produced[6] as shown in Fig. 1. The recent extensive study of silica-zirconia sol-gel resist[1] with different mixing ratios of Si:Zr showed a HTA-controlled calcination and formation of silica and zirconia nano-crystalline phases of cristobalite, zircon $ZrSiO_4$, monoclinic-ZrO_2, tetragonal-ZrO_2; e.g., ZrO_2 is material of ceramic knifes which become widely used as kitchen appliances over few past years. Controlled calcination is a direct invitation to make micro-optical elements[7] with different refractive indices. Moreover, photo-initiators, which help to have a larger 3D polymerisation window in 3D laser printing, are burned out in the calcination step leaving a pure glass/ceramic phase. At larger temperatures, precipitation of ceramic phases takes place with very rich possibilities to tailor final state of material composition and function for a specific application[8]. Concept of metamaterials is inherently linked to optical applications in domain of flat optics where amplitude, phase, polarisation, wavefront of light can be tailored at nanoscale by patterns of functional nanostructures and 2D materials. Also, optically active metamaterials can be created by localisation of light in surfaces waves - plasmons, which can provide a laser analog at nanoscale, the spaser[9]. In spaser, the optically active gain medium is deposited around a nanoparticle, similarly to a sphere-in-a-dye micro-laser concept with the cavity and active medium space-separated[10]. Definition of structures, patterns of different materials with nanoscale resolution is required for these applications in photonics. High-resolution lithography, which evolved as a planar 2D nanotechnology tool for micro-electronics is used and adopted for 3D nano-fabrication. It exemplifies a top-down approach, which has challenges when truly 3D metamaterials have to be produced.

A more practical approach is to use an inherently 3D direct laser writing, which can reach sub-100 nm

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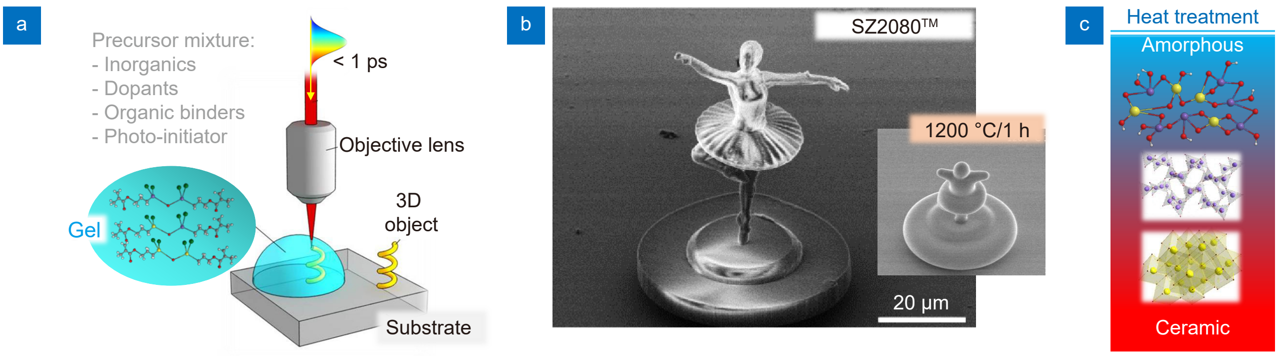

Fig. 1 | Top-down (**a**) and bottom-up (**b**) steps of nanomaterial synthesis. (**c**) Glass, crystalline, ceramic material is tuned via initial composition of a photo-curable precursor mixture and its thermal annealing at the required temperature, pressure, gas ambience. Surface tension driven reshaping is shown in scanning electron microscopy images in (b), where the same scale applies to both images before and after high temperature annealing.

resolution and high throughput in polymerisation via the top-down approach of 3D manufacturing[11]. By adding the HTA post-fabrication step[1], the second stage of self-organisation, i.e., the bottom-up character of material synthesis is harnessed. A polymerisable mixture of solid (e.g., nanoparticles) and liquid precursor materials including optically active dopants is prepared first (Fig. 1(a)), then 3D polymerised and by HTA step (b) it is guided to a glassy, noncrystalline or ceramic state with simultaneous decomposition of the organic part/binder[1,3,6].

Synthesis of new glass-ceramic materials via solid-solid phase transformations guided by surface tension at HTA stage, large surface area, which facilitates a fast diffusion of materials participating in chemical reactions and phase transformations is a new promising paradigm shift in material synthesis facilitated by ultra-short pulse lasers. Since the average power of the ultra-short pulse lasers follows the Moore's law from 2000[12], applications will benefit from a lower cost of photons. Glass transition, phase changes still have their surprises, e.g., crystal-to-amorphous phase changes in solids and liquid-to-solid phase transitions have their secrets as demonstrated recently for the average density ice[13]; it is noteworthy that 2022 was the year-of-glass, UNESCO. Further research in formation of glass and crystalline phases is required and can benefit from neutron scattering which has large penetration depth and is sensitive to light elements O and C redistribution.

Nano-structured glass-ceramic materials and composits are expected to find complimentary fields of applications to their metallic counterparts: metallic glasses and high-entropy alloys (crystalline), which have range of useful properties harnessed by technologies from biomedical to space and harsh environments in industry, where high temperatures, pressures, aggressive chemicals and radiation backgrounds are encountered.

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