

extinctions, wildlife extirpations, freshwater appropriation, ocean degradation, extractionist operations, and the production of industrial, pesticide, nitrogen, manure, plastic, and other waste—all unfolding amid climate-change ordeals.

In the face of this juggernaut, a singular focus on a techno-managerial portfolio seems fueled by a source other than pragmatism alone. That portfolio—which would include such initiatives as climate geoengineering, desalination, de-extinction, and off-planet colonization—is in keeping with the social rubric of human distinction. The prevalent corpus resonates with a Promethean impulse to sustain human hegemony while avoiding the most expeditious approach to the ecological predicament—contracting humanity's scale and scope by means that will simultaneously strengthen human rights, facilitate the abolition of poverty, elevate our quality of life, counter the dangers of climate change, and preserve Earth's magnificent biodiversity.

To pursue scaling down and pulling back the human factor requires us to reimagine the human in a register that no longer identifies human greatness with dominance within the ecosphere and domination over nonhumans. The present historical time invites opening our imagination toward a new vision of humanity no longer obstructed by the worldview of human supremacy. Learning to inhabit Earth with care, grace, and proper measure promises material and spiritual abundance for all. ■

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#### 3D PRINTING

# Printing nanomaterials in shrinking gels

Photopatterning of reactive sites in gels enables arbitrary patterning of nanoparticles

By Timothy E. Long and Christopher B. Williams

**T**he creation of nanoscale electronics, photonics, plasmonics, and mechanically robust metamaterials will benefit from nanofabrication processes that allow a designer full control in manipulating nanomaterial precursors in a programmable and volumetric manner. Despite decades of research, it remains challenging to design nanofabrication processes that can produce complex free-form three-dimensional (3D) objects at the scale of tens of nanometers. On page 1281 of this issue, Oran *et al.* (1) report on the photopatterning of reactive sites into water-swollen, chemically cross-linked acrylic gels for the subsequent site-specific deposition of nanomaterials and nanoparticles. After chemical and thermal dehydration, the gel scaffold holds the nanomaterials in a distinct 3D arrangement. This process, termed implosion fabrication (ImpFab) because the scaffold of the gel effectively “implodes” upon solvent removal, provides an opportunity to fabricate centimeter-scale assemblies of nanomaterials that possess multiple functionalities.

The macroscopic dimension of a solvent-swollen gel provides sufficient molecular mobility to host efficient chemical reactions. However, the utility of a covalently cross-linked gel as a “nanomanufacturing reactor” for the creation of programmable nanomaterials has remained unrealized until now. Top-down processes such as photolithography can create structures with spatial resolutions approaching tens of nanometers (2), but the fundamental process methodologies limit the creation of arbitrary geometries in three dimensions.

Researchers are now implementing bottom-up nanofabrication processes that are similar to more recent efforts in additive

manufacturing (often termed 3D printing), in that they can pattern materials in 3D space without a photomask (3). One such process, direct laser writing, is an exceptional process for the preparation of arbitrary 3D geometries (4, 5). Rastering femtosecond laser pulses through microscope optics into a photopolymer precursor enables selective photocuring anywhere in the material through the interaction of multiple photons to create discrete, polymerized voxels (3D pixels).

Although this technique creates 3D structures of any arbitrary geometry, its fabrication resolution is often limited by the wavelength of ultraviolet light to hundreds of nanometers (6, 7). Expanding the material selection for the process beyond electrical insulators has also proven challenging. Creating functional metallic materials with this process is only permitted through patterning polymer-particle nanocomposites (8), metal-coating the entirety of the printed surface, or multiphoton-induced reduction of metal ions. Postprocess coating does not allow for selective deposition and

“...Oran *et al.* avoid any detrimental interactions of nanoparticles during exposure...”

limits the geometries that are achievable (see the figure, right). Irradiating polymer composites and multiphoton-induced reduction of metal ions constrain resolution through refraction effects and the limited control of growth and aggregation during photoreduction, respectively (9).

As such, fabricating truly arbitrary 3D metallic shapes at the scale of tens of nanometers has yet to be demonstrated. Researchers remain challenged to circumvent the resolution and material selection constraints imposed by direct laser writing. Oran *et al.* combined the unusual volumetric reduction properties of water-swollen gels (hydrogels) and a templating approach to fabricate complex 3D metallic nanostructures at an unprecedented scale (see the figure, left). They leveraged the stable deswelling performance of a hydrogel in the context of metallic nanofabrication. In particular, they photopatterned water-swollen gels with two-photon laser direct writing to

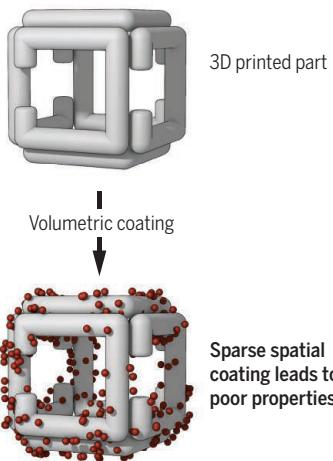
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## Precisely placing nanomaterials

The ImpFab method of Oran *et al.* enables selective nanomaterial compositions with 3D geometries rather than simply coating 3D printed parts.

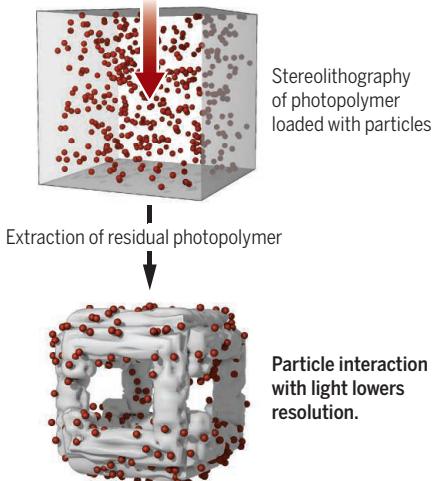
### Conventional coatings

Volumetric methods for coating 3D printed parts with nanoparticles yield poor results because the coverage is sparse and confined to the surface.



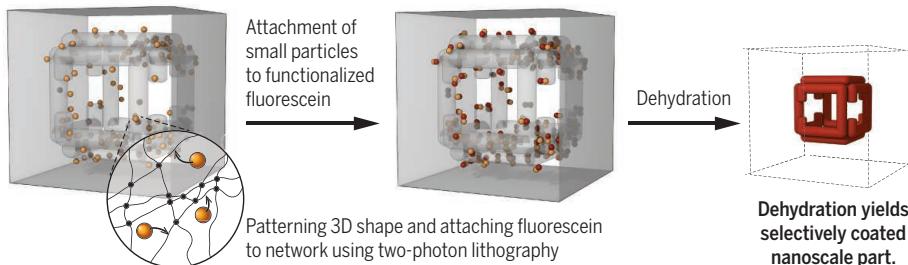
### Conventional lithography

Optical interactions between particles in photopolymer precursors and incident light lead to poor feature resolution because of the scattering of light from the nanoparticles.



### ImpFab processing

This method eliminates particle interactions with incident ultraviolet light and enables selective particle coating. The final dehydration step shrinks the gel in an implosive process.



create reactive sites that enable site-specific postprocess functionalization of nanomaterials and nanoparticles. Dehydration then rapidly shrinks the fabricated structure to 1/10 its original size.

Oran *et al.* build on earlier efforts that reported the efficient reaction of fluorescein with carboxylate-containing hydrogels during two-photon excitation (10). Their key realization was that fluorescein derivatives also potentially serve as chaperones for the concurrent introduction of functionality and create sites for subsequent colocation of nanomaterials. This multistep segregation of defining geometry and defining material ensures that the nanomaterials are not present during the patterning step. Thus, Oran *et al.* avoid any detrimental interactions of nanoparticles during exposure that can occur in mask-projection stereolithographic printing processes (see the figure, middle). Moreover, the addition of compounds after the initial conjugation of nanomaterials can

intensify the concentration of materials as well as form a spatially arranged multinanomaterial structure. Repetition of the process chain also allows the introduction of multiple nanomaterials as well as multiple patterns of nanomaterial structure.

The modularity of the methodology of Oran *et al.* for creating 3D patterns is an important aspect of their contribution. Writing into a 3D swollen gel and delivering a patterned array of functionality represent an important departure from traditional 2D and 3D lithographic printing where the patterned energy defines a printed photopolymer structure. This approach addresses a key challenge in 3D direct laser writing in terms of precisely depositing nanomaterials onto printed objects, versus the more prevalent stochastic introduction of nanoparticles that degrades both performance and printing resolution. Furthermore, two-photon laser writing allows for patterning energy with voxel-level control in 3D space, so the process

can create discontinuous shapes along the hydrogel surface.

Although direct laser writing is suitable for patterning materials onto substrates and in free-form shapes, the process cannot create discontinuous multimaterial structures at the resolution Oran *et al.* demonstrated. The precise delivery of nanomaterials in multiple, complex patterns that they report enables unprecedented formation of nanomaterials of controlled geometry and high performance. The process chain effectively separates geometry definition through direct laser writing, material definition through chemical templating and sintering, and pattern resolving through gel deswelling. Separation of these steps circumvents the traditional materials, resolution, and geometric complexity constraints imposed by existing nanofabrication processes.

The work by Oran *et al.* also creates opportunities for studying the influence of the molecular architecture of the gel. Gels are complex structures that can vary in chemical composition, molecular weight between cross-link points, and dangling chain ends, and in whether they are physical versus chemical networks. These parameters in structure will influence the precise location in the gel of reactive sites for two-photon excitation and also must be considered in efforts to expand the available photoinduced chemistries in the aqueous state. Extension to other materials only depends on developing deposition chemistry that can proceed at room temperature in aqueous media. Thus, the method developed by Oran *et al.* should allow researchers to consider a myriad of new materials and reaction pathways, including other semiconductors or metals. The ability to process free-form, multimaterial nanostructures with discontinuous nanowires will enable next-generation designs of photonic, electrical, and mechanical metamaterials, as well as microelectronics, actuators, and sensors. ■

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