

humans in depth. Using a chamber containing occupants and different concentrations of ozone, they measured the reactivity and concentration of  $\cdot\text{OH}$  and VOCs inside the chamber. In the absence of ozone, they found that  $\cdot\text{OH}$  mainly reacted with the isoprene from human breath, whereas when ozone was present, squalene in skin oil reacted with the ozone to produce species such as 6-methyl-5-hepten-2-one (6-MHO). They also observed that isoprene and products from its reaction with  $\cdot\text{OH}$  also react with ozone to produce more  $\cdot\text{OH}$ . All these observations point to the conclusion that humans are a net source of  $\cdot\text{OH}$  indoors. Using a three-dimensional model, the authors simulated the distribution of  $\cdot\text{OH}$  around the human body under different indoor conditions. They observed that the human body interacts with the indoor environment in an analogous manner to how Earth interacts with the atmosphere: Both the human body and Earth are chemical reactors, consuming or producing oxidants and oxidized species in their surrounding atmospheres.

Recent research, including that of Zannoni *et al.*, has raised awareness of the need to better understand specific processes that affect indoor air quality. How do human body functions directly influence indoor air, and how does this compare with the activities of humans indoors such as emissions from cooking or cleaning? Furthermore, it is also important to better understand how secondary chemicals and reactions in the indoor environment differ from those that occur in the atmosphere. For instance, it will be interesting to learn whether human emissions indoors interact with chemicals such as the nitrate radical, which is a key atmospheric oxidant during the nighttime outdoors but may be present during the daytime in dimly lit indoor environments (14, 15). These are open questions that need to be answered to better understand indoor air quality to ultimately provide better living and working environments. ■

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#### 3D NANOPRINTING

## 3D-printing nanocrystals with light

Nanocrystals are connected to form complex 3D structures by means of two-photon lithography



By Jia-Ahn Pan and Dmitri V. Talapin

**T**he ability to fabricate custom three-dimensional (3D) objects on demand has revolutionized prototyping and small-scale manufacturing processes. From low-cost filament extruders that a hobbyist can use to replace a plastic battery cover, to laser sintering machines for metal spacecraft parts, the reach of 3D printing technologies in low- and high-end markets continues to broaden. A crucial part of this progress has been the expansion of the library of materials that can be 3D-printed. Nanocrystals have many functional properties, but their integration with 3D printing has been limited, mostly relying on the use of polymer material as a scaffolding. On page 1112 of this issue, Liu *et al.* (1) demonstrate the 3D printing of nanocrystals using a method known as two-photon lithography. The intense beam of an infrared femtosecond laser induces simultaneous absorption of two photons in a very small volume, triggering photochemical reactions at nanocrystal surfaces.

Nanocrystals—nanometer-sized crystals of various inorganic materials—are widely studied as building blocks for functional materials because of their advanced mechanical, electronic, optical, and thermal properties (2). Their surfaces can be made

to repel or attract one another depending on the surface chemistry and external conditions. Thus, they can be suspended in liquids, forming what is known as a colloidal dispersion. Conversely, they can be made to aggregate, precipitating compact solids from the dispersion. This attraction-repulsion property allows for the useful functions of inorganic materials to be combined with the convenience of solution processability. After about three decades of research and development, there are now methods for preparing nanocrystals made of different semiconductors, metals, and many other technologically important materials.

This versatility has enabled nanocrystals to transcend the unfortunate fate of many academically promising nanomaterials that ultimately proved uncompetitive with established technologies in practical applications. For instance, nanocrystals are used as the color component in quantum dot light-emitting diode (QLED) televisions. Nanocrystals have shown impressive performance in optoelectronic components—e.g., in LEDs, infrared sensors, solar cells, smart windows, optical metamaterials, and thermoelectric elements, (3–5). Yet, there still exists a bottleneck for integrating nanocrystals into complex devices. The fabrication of such devices requires precise positioning of nanocrystals with respect to each other, as well as other electronic components.

For planar structures, inkjet printing and direct optical lithography of functional inorganic nanomaterials (6) have

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Nanocrystals are 3D printed without the use of a polymer scaffolding.

been used in manufacturing workflows. Optical lithography allows the placing of components with submicrometer resolution, thanks to ideas and tricks borrowed from traditional semiconductor fabrication. However, the arrangement of nanocrystals into arbitrary complex 3D structures has so far been out of reach.

A form of 3D printing of colloidal nanocrystals was demonstrated more than a decade ago (7), but this early approach requires mixing nanocrystals with photocurable organic materials. Exposure to light induces the formation of chemical bonds between the organic components to form the 3D solid while the nanocrystals are simply embedded in the polymer host. Although these hybrids have some useful properties of the organic components (e.g., flexibility), they also inherit less-desirable attributes, such as low electrical conductivity and poor thermal and mechanical stability. The most straightforward route to the fabrication of all-inorganic 3D structures is to use the aforementioned method and then burn off the organic components, as researchers have done through thermal annealing (8). Unfortunately, this high-temperature approach is restricted in chemical scope and induces substantial volume contraction that deforms the printed 3D objects (9). A polymer-free 3D printing approach requires a way to form strong chemical bonds between inorganic components and provide structural integrity without photoactive organic additives.

The study of Liu *et al.* demonstrates a chemical pathway that makes this solidification possible. The authors show that absorption of infrared laser light by cadmium selenide/zinc sulfide core-shell quantum dots or silver nanocrystals leads to the decomposition and detachment of surfactant molecules from the nanocrystal surfaces. This light-induced process triggers a series of chemical transformations that result in the aggregation of the nanocrystals into a densely packed solid with high overall inorganic content. By controlling the path of the focused laser beam, the authors were able to create a fully densified 3D object inside a nanocrystal solution. In their demonstration, sub-100-nm features were successfully printed, which is much smaller than the wavelength of the laser used. Normally, such a high resolution would not be possible because diffraction spreads out even the most tightly focused laser beam into an area comparable in size to the wavelength of the light. To go beyond this limit, the authors use a technique

known as the two-photon absorption process, in which absorption is only possible where the light intensity is at its highest. This shrinks the active volume to a region smaller than the wavelength of the light.

The optoelectronic properties of the quantum dots are preserved during this patterning process. Liu *et al.* also demonstrated the 3D printing of continuous structures made of different material compositions at different points, showing the versatility of this approach. This was achieved by sequential printing with two different nanocrystal solutions.

With a method to 3D print high-quality inorganic structures, future research should explore the patterning mechanism and nuances of the surface chemistry of various nanocrystals. Many questions about the 3D printing of colloidal nanocrystals will need to be answered, such as determining other classes of surface-bound molecules that can similarly detach or decompose upon photo-irradiation. The material properties of these 3D-printed structures, and therefore their utility in fabricating devices with competitive performance, also await characterization. Optimization of the optoelectronic performance of 3D-printed nanocrystals, such as photoluminescence quantum yield and charge mobility, would go a long way in this regard. In a different vein, reducing the minimum light intensity required for 3D patterning would allow this chemistry to be compatible with more cost-efficient 3D printing approaches, such as digital light processing.

The dream of a hobbyist and an engineer alike is a printer that builds complete, fully functional devices with both passive (e.g., casing, wiring, supports) and active components (e.g., sensors, transistors, LEDs) with the press of a button. Liu *et al.* bring this vision one step closer to reality by adding functional inorganic components made of nanocrystals to the library of 3D-printable materials. ■

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#### METAL FATIGUE

## Foreseeing metal failure from its inception

The life span of metals can be inferred from early microscopic deformation events

By Mostafa M. Omar and Jaafar A. El-Awady

In 1842, the axle of a locomotive traveling between Versailles and Paris suddenly snapped, leading to a fiery and fatal crash. Metal fatigue—the weakening and cracking of the material from cyclic loading—was the root cause of this accident. This tragedy likely spurred the first systematic research on this type of material failure (1). Almost two centuries later, metal fatigue remains a constant plague for mechanical systems today. Fatigue can cause failure even if the loads did not result in any macroscopic deformation. This behavior is known to be sensitive to the tiniest defects in the material; hence, an accurate prediction of fatigue failure remains elusive. On page 1065 of this issue, Stinville *et al.* (2) present a physics-informed approach in which the fatigue strength of a metallic material can be predicted from measurements after only a single cycle of loading.

One basic example of metal fatigue is bending a metal paperclip repeatedly until it breaks. If the bent region on the paperclip is carefully inspected before failure, one would notice a change in its surface roughness. This is a manifestation of increased irreversible slip localization on the surface (see the figure), which is induced by the motion of dislocations. In more technical terms, under loading, metals deform by the motion of linear defects known as dislocations, which cause the atoms to slip over each other. Surface slip localizations are stress concentration sites. These locations act as nucleation sites for cracks that can progressively grow with further cyclic loading and eventually lead to failure.

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