Printing Precise Materials with Visible Light

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A three-component system uses four different wavelengths of visible light to rapidly print 3D materials with versatile mechanical properties and precise feature sizes.

The expansion of 3D printing has rapidly innovated product creation, from design conception to end-stage manufacturing. In this issue of ACS Central Science, Page and co-workers further advance 3D printing technologies by developing a coinitiator system that allows efficient printing with visible light.1 Previous innovations have allowed printed materials to become ubiquitous in both academic and industrial settings, including construction, prototyping, customizable medical devices, and even affordable housing. 3D printing, or additive manufacturing, typically involves successive layering of materials on top of one another. These materials are wide-ranging and include ceramics, metals, nanomaterials, polymers, or composites. While polymeric materials are commercially attractive due to their low cost, scalability, structural modularity, and ease of processing, challenges include low resolution, high energy consumption, and slow speeds. Ideally, these polymerizations need to be both fast and spatiotemporally controlled such that one can choose when and where to initiate a polymerization that converts liquid monomer into solid polymer. Toward these ends, photopolymerizations have garnered a great deal of scientific interest, wherein light is used as a trigger to initiate polymerizations that proceed rapidly.

Engineering advancements have enabled light-driven 3D printing to have the fastest speeds and highest resolution of the current 3D printing processes. However, present-day efforts largely rely on ultraviolet irradiation (Figure 1). While this high-energy light (<400 nm) is often chosen for its ability to rapidly cross-link (or “cure”) polymeric chains, it is not without its limitations. Notably, it suffers from material degradation, limited monomer functional group tolerance, and thin layer penetration due to UV light either absorbing or scattering before reaching the intended target. To address these concerns, the use of a milder, cheaper, and low-energy visible light is an appealing alternative but is typically precluded by the opposite problem: slow speeds. Here, Page and co-workers report a three-component photosensitizer coinitiator method that allows visible light LEDs to rapidly print 3D materials (Figure 1).1 Excitingly, this system can be tailored to different wavelengths of light through simple exchange of the photosensitizer to print materials with varied stiffness and precise resolution using four different wavelengths of visible light.

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Figure 1. Traditional additive manufacturing is performed with high-energy ultraviolet LEDs that suffer from challenges including shallow penetration depths, biocompatibility issues, and limited functional group tolerance. In the highlighted article, Page and co-workers establish a versatile platform using visible light LEDs for rapidly printing 3D materials.
When using low-energy visible light, a historical limitation is access to appropriate photoinitiator (PI) or photosensitizer (PS) systems. However, the recent renaissance in visible light catalysis has expanded this toolkit dramatically, with contributions in disparate fields such as organic synthesis, chemical biology, cancer therapy, and materials science. While visible-light-promoted photopolymerizations have been accomplished as recently reviewed, such systems relied on multistep energy/electron transfers that suffer from impracticalities including slow cure times and high irradiation intensities.

To overcome these limitations, Page and co-workers implement a three-component system: a PS and two donor/acceptor coinitiators that serve to promote PS regeneration and double the radicals produced for each photon absorbed. For each LED (red, 615 nm; green, 525 nm; and blue, 460 nm), a wavelength-appropriate PS is chosen along with an inert opaquing agent (OA, Figure 2A). The OA helps to control resolution and cure homogeneity—properties that could otherwise be challenging with deeper penetrating light. Optimization of compound concentrations and engineering considerations (e.g., exposure times) was performed for each system through an elegant process termed “resolution print” (Figure 2B). Here, an object is printed that contains 12 squares that (i) vary in exposure time and (ii) contain smaller features (1–16 pixels) to characterize resolution. Thus, each resolution print gives information about how different exposure times affect lateral and vertical resolution for a given concentration of OA that allows these parameters to be optimized quickly for a given wavelength of light. Materials can, therefore, be printed with rapid build speeds in wide processing windows and optimal x-, y-, z-resolution in small features.
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The mechanical properties of an object depend not only on its parts but also on the way those parts are put together as defined by the manufacturing process. The directional dependence of a mechanical property, termed mechanical anisotropy, has been called the “largest problem in additively manufactured parts”, as layer-by-layer production creates heterogeneity between the build direction and its parallel plane. After determining that the three-component system did not alter mechanical performance, Page and co-workers sought to investigate the integrity of the material when printed at three different angles: horizontal, vertical, and diagonal. Strikingly, the printed dogbones shared a nearly identical stiffness at varying levels of strain indicating that the layer-by-layer production did not contain defective boundaries. Instead, stiffness could be predictably controlled by simple monomer and cross-linker selection. By reducing the amount of chosen cross-linker and exchanging a “hard” monomer with a comparatively “soft”, hydrophilic monomer, the stiffness of printed materials could be reduced by 3 orders of magnitude while swelling in water was enhanced 3-fold (Figure 2C). In the future, one could imagine that multifunctional materials with disparate mechanical properties could be printed with this system using different monomers and orthogonal LED sources. Finally, a complex 3D octet truss was printed to demonstrate that higher-order structures could be printed with rapid build speeds in wide processing windows and optimal x-, y-, z-resolution in small features.

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The modular platform for 3D printing described herein is primed for further expansion and optimization. Some current challenges to overcome include the oxygen sensitivity of PS that necessitates printing under inert gases and the colored additives that currently prevent printing transparent objects. There are numerous, exciting avenues to explore including merging orthogonally triggered photocontrolled polymerizations and multiwavelength additive manufacturing to facilitate wavelength-selective 3D printing with solely visible light. Toward the latter, recent work by the Page lab establishing structure–property relationships between photocatalysts and polymerization metrics may provide a stepping stone. A clear advancement would be to move even further into the near-infrared region to enhance penetration depth and enable printing larger, multicolor objects. Finally, the residual PS observed by Page and co-workers may ultimately allow modified functional plastics to find utility in applications such as photodynamic therapy or living additive manufacturing. The future of visible light 3D printing is certainly colorful and bright!

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