change to the GATOR2 binding site via movement of helix C3 (Fig. 5D). Alternatively, a segment of the partially disordered linker domain, which contacts the leucine-binding pocket via Leu261 in helix L1 (Fig. S3A), is also in close proximity to the GATOR2 binding site in our structure (Fig. 5C). Therefore, changes in the leucine-binding state of Sestrin2 from GATOR2 will probably require ascertaining the structure of either apo-Sestrin2 or the Sestrin2–GATOR2 complex. Furthermore, understanding the mechanism by which Sestrin2 inhibits the mTORC1 pathway awaits the elucidation of the availability of the GATOR2 binding site.

Despite these insights, several important questions remain. Fully understanding how leucine binding causes dissociation of Sestrin2 from GATOR2 will probably require ascertaining the availability of the GATOR2 binding site. To this end, we performed an in vitro competition binding assay to determine the availability of the GATOR2 binding site. We first determined the approximate affinity of Sestrin2 for GATOR2 by measuring the dissociation constant (Kd) of the Sestrin2–GATOR2 complex. We then incubated the Sestrin2–GATOR2 complex with increasing concentrations of leucine, and measured the proportion of Sestrin2–GATOR2 that dissociated from GATOR2. The results of this assay are shown in Fig. 6A. The Kd of the Sestrin2–GATOR2 complex is approximately 3 μM, and the dissociation constant of Sestrin2 for GATOR2 decreases linearly with increasing leucine concentration, indicating that leucine binding causes dissociation of Sestrin2 from GATOR2.

The extremely high melting point of many ceramics adds challenges to additive manufacturing as compared with metals and polymers. Because ceramics cannot be cast or machined easily, three-dimensional (3D) printing enables a big leap in geometrical flexibility. We report preceramic monomers that are cured with ultraviolet light in a stereolithography 3D printer or through photochemical polymerization of polymeric precursors, forming 3D ceramic structures that can have complex shape and cellular architecture. These polymer structures can be pyrolyzed to a ceramic with uniform shrinkage and virtually no porosity. Silicon oxycarbide microlattice and honeycomb cellular materials fabricated with this approach exhibit higher strength than ceramic foams of similar density. Additive manufacturing of such materials is of interest for propulsion components, thermal protection systems, porous burners, microelectrochemical systems, and electronic device packaging.

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**SUPPLEMENTARY MATERIALS**

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Materials and Methods

Figs. S1 to S6

Table S1

References (30–44)

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**REPORTS**

3D PRINTING

Additive manufacturing of polymer-derived ceramics

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The extremely high melting point of many ceramics adds challenges to additive manufacturing as compared with metals and polymers. Because ceramics cannot be cast or machined easily, three-dimensional (3D) printing enables a big leap in geometrical flexibility. We report preceramic monomers that are cured with ultraviolet light in a stereolithography 3D printer or through photochemical polymerization of polymeric precursors, forming 3D ceramic structures that can have complex shape and cellular architecture. These polymer structures can be pyrolyzed to a ceramic with uniform shrinkage and virtually no porosity. Silicon oxycarbide microlattice and honeycomb cellular materials fabricated with this approach exhibit higher strength than ceramic foams of similar density. Additive manufacturing of such materials is of interest for propulsion components, thermal protection systems, porous burners, microelectrochemical systems, and electronic device packaging.

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BN, AlN, SiOC, SiCN, BCN, or other compositions, whereas volatile species (CH₄, H₂, CO₂, H₂O, and hydrocarbons) leave the material. Preceramic polymers are currently used to synthesize ceramic fibers and to densify ceramic matrix composites by infiltration. Two-dimensional photolithography and soft lithography have been demonstrated (6, 7). The absence of a sintering step enables lower synthesis temperatures without the need for pressure, as compared with classical ceramic powder processing, and the absence of sintering additives results in improved thermomechanical properties (8). By attaching thiol, vinyl, acrylate, methacrylate, or epoxy groups to an inorganic backbone such as a siloxane, silazane, or carbosilane, ultraviolet (UV)-active preceramic monomers can be obtained (7, 9). Two different additive manufacturing techniques based on photopolymerization can be used to achieve spatial control. For conventional stereolithography (SLA), sufficient polymerization inhibitor and UV absorber are added to the resin formulation to confine the polymerization to the laser exposure point and to minimize scatter to maintain fidelity in the features of the printed part. UV light is then scanned across the resin surface to expose a cross section and build up a thin slice (30 to 100 μm) of the part to be manufactured. Although almost any geometry can be fabricated with this approach, the process is slow, because every 30- to 100-μm thin layer has to be exposed separately. Structures with linear features extending from the exposure surface, such as lattices and honeycombs, can be formed 100 to 1000 times as rapidly as with the self-propagating photopolymer waveguide technology (SPPW) (10, 11). Monomers are selected to promote a change in the index of refraction upon polymerization, which causes internal reflection of the UV light, trapping it in the already-formed polymer. This exploits a self-focusing effect that forms a polymer waveguide, tunneling the light toward the tip of the waveguide and causing it to polymerize further. This reduces the need for additives that control scatter and UV absorption. The architecture of the material or structure can then be defined by a patterned mask that defines the areas exposed to a collimated UV light source (10).

Both methods produce parts consisting of cross-linked polymer (Fig. 1), where the cross-link density depends on exposure parameters and can be increased by thermal treatments or additional UV exposure. Unpolymerized resin can be recycled and reused.

The configuration and microstructure of the preceramic polymer determine the composition, microstructure, and yield of ceramic after pyrolysis. A high cross-link density is necessary to prevent the loss of low-molecular mass species and fragmentation during pyrolysis. Siloxane-based polymers with their Si-O-Si backbone result in silicon oxycarbides, whereas silazanes introduce nitrogen due to their Si-N-Si backbone. Combining siloxanes with silazanes results in a SiOCN ceramic after pyrolysis. The addition of silane compounds typically reduces the amount of oxygen and pushes the ceramic composition toward SiC (8). The ratio of carbon in the final ceramic can be tailored by adding phenyl groups on the side chain of the polymer or using a carbon-based cross-linking agent such as divinyl benzene. The precursor chemistry can also be changed to incorporate other elements—for example, B or Zr to enhance temperature capability (12); Fe, Co, or Ni to introduce magnetic properties; or Cu, Pd, or Pt for catalytic properties (13). To fabricate the structures shown in Fig. 1 a UV-curable siloxane resin system was formulated by mixing (mercaptomethyl) methylsiloxane with vinylmethoxysiloxane and adding UV-free-radical photo initiator, free-radical inhibitor, and UV absorber. The resulting liquid resin was used in a benchtop stereolithography 3D printer (Formlabs Form 1+). To fabricate the larger microlattice and honeycomb structures via SPPW for mechanical testing, the resin was reformulated without UV absorber, poured into a DELRIN reservoir, and exposed with UV light through a patterned mask (see the supplementary materials for details).

Pyrolysis at 1000°C in argon was accompanied by 42% mass loss and 30% linear shrinkage. The resultant ceramic is amorphous, as ascertained by x-ray diffraction (XRD) and transmission electron microscopy (TEM), and has a composition of 26.7 atomic percent (at %) Si, 33.4 at % C, 4.1 at % S, and 35.8 at % O, or SiO₁.₃₄C₁.₂₅S₀.₁₅ as measured by inductively coupled plasma mass spectrometry. The ceramic structures fabricated are fully dense, with no porosity or surface cracks observed by scanning electron microscopy and TEM (Fig. 2). Ceramic parts fabricated with the self-propagating photopolymer waveguide process exhibit a very smooth surface (Fig. 2A), whereas parts fabricated by stereolithography show the typical steps at the surface from the layer-by-layer printing process (Fig. 2C). As the undulations could act as stress concentrators and negatively affect the mechanical properties, all mechanical tests were performed on parts fabricated by SPPW. The SiOC ceramic fractures in a conchoidal manner typical for brittle amorphous materials, with curved breakage surfaces and ripples (Fig. 2B). To avoid shattering on pyrolysis, the printed polymer structure is typically limited to features with less than ~3 mm in thickness in one dimension and the heating rate to less than 20°C/min, so that evolving gases can escape. By selecting appropriate cellular architectures, large

![Fig. 1. Additive manufacturing of polymer-derived ceramics.](http://science.sciencemag.org/content/351/6268/59/F1)

(A) UV-curable preceramic monomers are mixed with photoinitiator. (B) The resin is exposed with UV light in a SLA 3D printer or through a patterned mask. (C) A preceramic polymer part is obtained. (D) Pyrolysis converts the polymer into a ceramic. Examples: (E) SLA 3D printed cork screw. (F and G) SPPW formed microlattices. (H) Honeycomb.
ceramic structures can be fabricated, with the size only limited by the equipment. This fabrication process introduces no noticeable gradients in composition, and temperature gradients can be mitigated by the cellular architecture, resulting in remarkably uniform shrinkage during pyrolysis. The shape of the polymer structure is therefore maintained well and the shrinkage can be predicted, as long as any surfaces in contact with the structure during pyrolysis are lubricated to prevent sticking. Various cellular architectures have been demonstrated with the self-propagating photopolymer waveguide process, including microspheres with densities of 0.22 to 0.35 g/cm³ (Fig. 1G), honeycombs with densities of 0.3 to 0.8 g/cm³ (Fig. 1H), and pyramidal truss cores with graded density (Fig. S4C).

Compression and shear testing was performed on as-pyrolyzed silicon oxycarbide structures, and the results are summarized in Fig. 3 and table S1. A compressive failure strength of 163 MPa was measured on a honeycomb structure with a density of 0.8 g/cm³ using a prescribed displacement rate of 10 μm/s. Shear testing was performed on four microlattices with densities of 0.22 to 0.35 g/cm³ according to ASTM C273, using a single lap shear test fixture, and resulted in ultimate shear strengths in the range of 3.7 to 4.9 MPa and modulus values of 830 to 1570 MPa. Failure in compression was catastrophic by sudden brittle fracture, whereas failure in shear was gradual by successive brittle fracture of single struts. The mechanical properties of silicon oxycarbide microlattice structures are compared to those of ceramic foams of similar density (Fig. 3). Noteworthy is the ~10 times higher compressive strength as compared with commercially available SiC foams (Duocel) and aluminosilicate foam (ceramic insulation) (table S2), as well as silicon oxycarbide foams (14). The improvement in shear strength does not appear as large in Fig. 3B because the values reported for SiC and aluminosilicate foams are flexural strength, which is measured by a bending test and is generally higher. Even in comparison to state-of-the-art cellular sandwich core materials, aluminum alloy honeycomb (HexWeb) and closed-cell polymer foam (Divinycell), the polymer-derived ceramic cellular materials look favorable. Sample details and measurement results are summarized in table S1.

The mechanical properties of a cellular material depend on the mechanical properties of the solid constituent material, the relative density of the cellular material, and the cellular architecture (i.e., the spatial configuration of voids and solid). Two factors contribute to the observed high strength. First, the ordered, periodic architectures are inherently more mechanically efficient than a random foam architecture. Gibson and Ashby (15) have described the general relationships for the elastic modulus (E) and failure strength (σ) of a cellular material as

\[
E \approx C_1 (E_s) \left(\frac{\rho}{\rho_s}\right)^{n_1}
\]

\[
\sigma \approx C_2 (\sigma_s) \left(\frac{\rho}{\rho_s}\right)^{n_2}
\]

The terms E₀ and σ₀ are the elastic modulus and representative failure strength of the solid material, respectively. The term ρ/ρₛ is the relative density of the cellular material, which is defined as its density (ρ) divided by the density of the solid constituent material (ρₛ). ρₛ of SiOC is 2.05 g/cm³. The proportionality constants C₁ and C₂ are related to the geometric configuration of the cellular material with respect to the loading direction. The exponents n₁ and n₂ are 2 and 1.5, respectively, for foams, where the cell struts exhibit bending-dominated deformation during elastic loading (15). Conversely, a lattice material can exhibit stretching-dominated deformation, when the lattice members are configured so that they are loaded either in tension or compression, which results in much-improved mechanical properties that decrease linearly with density (n₁ = 1 and n₂ = 1). The ceramic microlattices exhibit a scaling n₂ = 1.06 (R² = 0.88), and the honeycombs show n₂ = 1.18 (R² = 0.99), demonstrating stretching-dominated mechanical performance. The difference in compressive strength arising from the different scaling of stretch-dominated versus bending-dominated architecture should be a factor of 3.2 at a relative density of 10% and increases to 5.8 at 3%. The proportionality constant C₂ for a brittle foam is ~0.2 (15), whereas the constant is estimated to be

![Fig. 2. Electron microscopy characterization of SiOC microlattice and cork screw. (A) SPPW-formed lattice node showing smooth surface. (B) Fracture surface of a strut. (C) SLA printed corkscrew showing undulations on the surface. (D) 3D printing step size is 50 μm. (E) Bright-field TEM image showing no porosity. (F) TEM diffraction indicating amorphous structure.](http://science.sciencemag.org/)
1/3 for microlattices (16), 0.87 for pyramidal truss structures (16), and 1 for honeycombs, accounting for additional increases in strength.

This high intrinsic strength is the second factor besides the architecture contributing to the much higher strength of these cellular materials as compared with previously reported ceramic foams. The higher strength of these cellular materials as compared with other ceramic materials, especially when derived from conventional powder routes. Ultimate strength values are measured as compared with other ceramic materials, especially when derived from conventional powder routes. Ultimate strength values with a tighter distribution are obtained, but due to the brittle nature of the material, they coincide with the yield and fracture strength.

To calculate the modulus of the solid constituent SiOC material, the equation for shear modulus of microlattices (17) is used

\[ G = \frac{E}{8} \sin^2\left(\frac{\pi}{8}\right) \frac{\rho}{p_i} \]  

where \( E \) is Young's modulus of 102 ± 26 GPa is obtained, which is in the range reported for similar compositions (5).

The silicon oxycarbide family of polymer-derived ceramics has demonstrated excellent high-temperature properties, including remarkable resistance to crystallization, oxidation, and creep (8, 18). These properties have been ascribed to the amorphous material exhibiting nanodomains of silica tetrahedra that are encased in a network of graphene (19). The heart of the 1- to 3-nm domains is formed by silicon-oxygen tetrahedra, and the interdomain boundaries consist of layers of \( sp^2 \) carbons. Silicon atoms bonded to one or two carbons substituted for oxygen make up the interface between silica domains and graphene walls (19).

The silicon oxycarbide microlattice structures showed excellent stability at high temperatures in air. At 1300°C, the structures gained ~0.15% mass over 10 hours, and most of this mass gain occurred within the first 2 hours. It is hypothesized that this is associated with a replacement reaction at the SiOC surface, creating an amorphous \( SiO_2 \) oxide layer and releasing CO or CO\(_2\). This oxide growth was qualitatively observed as a shift in interference coloration at the microlattice surface. After each subsequent heat treatment, there was a shift in iridescent coloration associated with increased thickness of the clear and thin (100 to 1000 nm) oxide scale, consistent with thin-film interference coloration. At 1400°C, the samples showed a slow but steady mass decline of ~1% after 10 hours. This mass loss was attributed to the "burn off" of free carbon in the SiOC structure (20). After 10 hours at 1400°C, a hazy surface oxide was observed. This oxidation product was characterized to be cristobalite by XRD. A similar behavior was observed at 1500°C, 1600°C, and 1700°C, albeit with an increasing mass loss rate and more pronounced cristobalite oxidation products (Fig. 4C). The highest temperature to which SiOC samples were exposed was 1700°C, and no degradation other than surface oxidation was observed. The mass loss is normalized by the surface area (Fig. 4A). The change in oxide structure is attributed to the oxidation product being amorphous at or below 1300°C, whereas above 1400°C it crystallizes to cristobalite. \( O_2 \) diffusion into the bulk oxidizes available free carbon, and at even higher temperatures, carbothermal reduction of \( SiO_2 \) from free carbon in the structure begins (20). The oxide shell on the surface appears to slow these reactions by limiting diffusion.
of the O$_2$ into the structure and CO$_2$ products out of the bulk. Upon cooling, there is a phase change with 7% volume change in the cristobalite (22), as well as a large shift in coefficient of thermal expansion (22), which leads to a cracked surface oxide. Upon reheating, the oxidation appears to restart underneath the cracked oxide layer, leading to a multilayer oxide scale after several heat treatments. X-ray diffraction did not detect phases other than cristobalite, indicating that bulk crystallization products, specifically β-SiC, were not present or were below the detection limit due to their small size and volume fraction (Fig. 3F). TEM of a sample heat-treated for 10 hours at 1300°C followed by 10 hours at 1500°C revealed the onset of bulk crystallization with scattered β-SiC crystals <$10$ nm inside the amorphous matrix. A lamella was milled out of a fractured surface of a microlattice strut, as indicated by the rectangle in Fig. 4c, so that oxide and SiOC base material could be analyzed (Fig. 4d). Bright-field images showed small crystallites of a few nanometers in size in both the oxide and SiOC region. High-resolution imaging could identify the crystallites as graphite and β-SiC, based on the lattice spacing and diffraction pattern (Fig. 4e). The small size of 5 to 10 nm of the crystals and the high fraction of remaining amorphous matrix indicate that crystallization had just started. The crystallites in the silicon oxide region are even smaller (Fig. 4f), consistent with the recent formation of this oxide region. Larger crystals are probably present in older oxide layers further from the interface, contributing to the cristobalite diffraction pattern recorded by XRD below. Note-worthy were small pores in the SiOC region that were not observed before the heat treatments and presumably developed due to carbon leaving as CO or CO$_2$ gas.

This indicates that the amorphous SiO$_{1.34}$C$_{1.25}$S$_{0.15}$ is more stable than other silicon oxycarbide compositions, which crystallize sooner (23). The high-temperature stability with respect to mass change in air is compared with other materials in Fig. 4b (mass change was extrapolated from reported mass versus time curves after 1 hour exposure in air). The silicon-oxycarbide structures show better oxidation performance than silicon oxycarbide materials from previous studies, which used different starting precursors, compositions, and pyrolysis temperatures (20, 24, 25). Silicon oxycarbide is more resistant to oxidation than SiC and Si$_3$N$_4$ and has been investigated as oxidation protection coating for these materials (6).

Various ceramic compositions can be processed with our approach, including materials that are difficult to form via sintering of powders, such as SiOC, Si$_3$N$_4$, and SiC ceramics. In this demonstration, we focused on structures out of silicon oxycarbide, and our cellular SiOC materials exhibit strength 10 times as high as commercially available ceramic foams of similar density and survive temperatures of 1700°C in air with surface oxidation. Such cellular ceramic materials are of interest for the core of lightweight, load-bearing ceramic sandwich panels for high-temperature applications—for example, in hypersonic vehicles and jet engines. Stereolithography of ceramics will open opportunities for complex-shaped, temperature- and environment-resistant ceramic structures from the microscale—e.g., in microelectromechanical systems (MEMS) or device packaging—to the macro scale—e.g., in propulsion or thermal protection systems.

REFERENCES AND NOTES


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SUPPLEMENTAL MATERIALS

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MATERIALS AND METHODS

Figs. S1 to S4
Tables S1 to S3
References

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BLACK HOLE PHYSICS

A radio jet from the optical and x-ray bright stellar tidal disruption flare ASASSN-14li

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The tidal disruption of a star by a supermassive black hole leads to a short-lived thermal flare. Despite extensive searches, radio follow-up observations of known thermal stellar tidal disruption flares (TDFs) have not yet produced a conclusive detection. We present a detection of variable radio emission from a thermal TDF, which we interpret as originating from a newly launched jet. The multiwavelength properties of the source present a natural analogy with accretion-state changes of stellar mass black holes, which suggests that all TDFs could be accompanied by a jet. In the rest frame of the TDF, our radio observations are an order of magnitude more sensitive than nearly all previous upper limits, explaining how these jets, if common, could thus far have escaped detection.

Although radio jets are a ubiquitous and well-studied feature of accreting compact objects, it remains unclear why only a subset of active galactic nuclei (AGNs) are radio loud. A stellar tidal disruption flare (TDF) presents a novel method with which to study jet production in accreting supermassive black holes. These flares occur after perturbations to a star’s orbit have brought it to within a few tens of Schwarzschild radii of the central supermassive black hole and the star gets torn apart by the black hole’s tidal force. A large amount of gas is suddenly

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Printing ceramics into complex shapes
Some materials, such as thermoplastics and metals, are naturally suited to being 3D printed because the individual particles can be fused together by applying heat. In contrast, ceramics do not fuse together the same way. Eckel et al. developed a way to pattern specific preceramic monomers using either 3D printing or stereolithography into complex, curved, and porous shapes. Upon heating, they observed almost no shrinkage, and the formed parts showed exceptional thermal stability.
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