LOW-DENSITY MATERIALS

Strong, lightweight, and recoverable three-dimensional ceramic nanolattices

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Ceramics have some of the highest strength- and stiffness-to-weight ratios of any material but are suboptimal for use as structural materials because of their brittleness and sensitivity to flaws. We demonstrate the creation of structural metamaterials composed of nanoscale ceramics that are simultaneously ultralight, strong, and energy-absorbing and can recover their original shape after compressions in excess of 50% strain. Hollow-tube alumina nanolattices were fabricated using two-photon lithography, atomic layer deposition, and oxygen plasma etching. Structures were made with wall thicknesses of 5 to 60 nanometers and densities of 6.3 to 258 kilograms per cubic meter. Compression experiments revealed that optimizing the wall thickness-to-radius ratio of the tubes can suppress brittle fracture in the constituent solid in favor of elastic shell buckling, resulting in ductile-like deformation and recoverability.

Lightweight structures that are both strong and tough may be engineered by utilizing such hierarchical design principles. The yield strength and stiffness of cellular structures scale as $\sigma_\text{f} \sim \sigma_\text{rel} \pi^n$ and $E \sim E_\text{rel} \pi^m$, where $\pi$ is the relative density, $\sigma_\text{rel}$ and $E_\text{rel}$ are the yield strength and stiffness of the parent solid, and exponents $n$ and $m$ are functions of the architecture (17). Cellular geometries that typically lead to the highest strength are stretching-dominated, meaning that they have no intrinsic mechanisms that allow for bending of the individual truss members (18, 19). The yield strength and stiffness of an ideal stretching-dominated structure scale linearly with relative density as $\sigma_\text{f} \sim \pi$ and $E \sim \pi^3$. This is in contrast to architectures that are either periodic and bending-dominated, whose modulus scales as $E \sim \pi^5$, or stochastic, with $E \sim \pi^9$ scaling (20).

We created a strong, stiff, and energy-absorbing hollow-tube nanolattice with an octet-truss geometry (Fig. 1) that consists solely of a brittle ceramic, aluminum oxide (alumina), and exhibits nearly full recoverability after compressions in excess of 50% strain. Nanomechanical experiments reveal that the Young's modulus of our nanolattices scales with relative density as $E \sim \pi^{1.61}$, and failure strength scales as $\sigma_\text{f} \sim \pi^{3.36}$, which differ from the analytical scaling for both stretching- and bending-dominated structures because of the hollow tubes and nodes.

Creation of ceramic nanolattices begins with the design and writing of a three-dimensional (3D) polymer scaffold using two-photon lithography direct laser writing. A thin alumina film is then deposited onto the polymer scaffold by atomic layer deposition (ALD), so that it coats the entire surface. The outermost walls of the coated structure are then removed by focused ion beam milling (FIB), and the internal polymer is etched away in O$_2$ plasma. The resulting 3D freestanding ceramic nanolattice consists of a network of hollow tubes, as shown in Fig. 1. This fabrication
method enables the creation of 3D structures with numerous geometries (8, 22). Further fabrication details and a schematic of the deposition process can be found in (23) and are shown in fig. S1.

Nanolattices in this work were designed with relative densities spanning \( \rho = 0.21 \) to 8.6%. Using a reported value for the density of ALD alumina, \( \rho_a = 2900 \text{ kg/m}^3 \) (24), the absolute densities of nanolattices were calculated to be \( \rho = 0.1 \) to 249 kg/m\(^3\), which places the lightest ones into the ultralight regime, defined as materials with densities \( \leq 50 \) kg/m\(^3\) (27). This density range is comparable to that of aerogels (25) and other ultralight materials (7, 27). In this work, nanolattices were designed to have tube wall thicknesses \( t \) of 5 to 60 nm, tube major axis \( a = 0.45 \) to 1.38 \( \mu \)m, and unit cell widths \( L = 5 \) to 15 \( \mu \)m (Fig. 1, B and C). A list of the parameters and relative densities is provided in Table S1.

Monotonic and cyclical uniaxial compression experiments were performed on nanolattices in a G200 XP Nanoindenter (Agilent Technologies). In the first set of experiments, structures were compressed uniaxially to \( \sim 50\% \) strain at a rate of \( 10^{-3} \text{ s}^{-1} \) to determine their yield stress and overall deformation characteristics (Figs. 2; 3, A to D; and 4, B and D; and fig. S2A). In the second set of experiments, structures were cyclically loaded and unloaded three times to \( \sim 70\% \) of their failure load, and unloading slopes from each cycle were averaged to estimate Young's modulus (Fig. 4, A and C, and fig. S2B). Unloading rather than loading moduli were used to mitigate the possible effects of loading imperfections such as misalignment and partial initial contact (fig. S2B). Additional samples were compressed in an in situ nanomechanical instrument, InSEM (Nanomechanics Inc.), to observe local and global deformation characteristics and to investigate the failure modes that occurred during deformation (movies S1 to S3). Stress-strain data and still frames of the in situ compression experiments are shown in Fig. 2.

Two distinct deformation signatures were observed during nanolattice compressions. These are best characterized using the thickness-to-radius ratio of the tubes, \( t/a \), as a figure of merit. Transmission electron microscopy (TEM) analysis revealed ALD alumina to contain 2- to 10-nm nanocrystalline precipitates intermixed in an amorphous matrix (Fig. 1F). A list of the parameters and relative densities is provided in Table S1.

Fig. 2. Compression experiments on thick- and thin-walled nanolattices. (A to E) Mechanical data and still frames from the compression test on a thick-walled \((L = 5 \mu \text{m}, a = 650 \text{ nm}, t = 10 \text{ nm})\) nanolattice demonstrating the slow, ductile-like deformation, local shell buckling, and recovery of the structure after compression. (F to J) Mechanical data and still frames from the compression test on a thin-walled \((L = 5 \mu \text{m}, a = 790 \text{ nm}, t = 50 \text{ nm})\) nanolattice showing catastrophic brittle failure and no post-compression recovery.
deformation, depending on the stress state that arises in the beams during loading. Elastic deformation and potentially recoverability will occur in a structure when the stress necessary to initiate these processes is below the critical stress required for fracture. The condition for elastic deformation can be determined by calculating the transition point between two pairs of failure modes: shell buckling versus fracture, and Euler buckling versus fracture. Equating the stresses necessary to initiate each individual failure mechanism, we obtain an expression for the critical transition point between fracture and elastic failure [see (20) for the full derivation]

\[ \left( \frac{t}{a} \right)_{\text{crit}} = \frac{\sigma_{fs}}{E} \sqrt{3(1 - v^2)} \]  

(1)

\[ \left( \frac{a}{L} \right)_{\text{crit}} = \frac{3}{\pi} \sqrt{\frac{2\sigma_{fs}}{5E}} \]  

(2)

Both of these functions depend on the constituent material properties: Young’s modulus (E), fracture strength (\(\sigma_{fs}\)), and Poisson’s ratio (v). Equation 1 represents the critical ratio between the wall thickness (t) and the major radius (a) that is necessary to induce a transition between local buckling and fracture in the tubes. Equation 2 represents the critical ratio between the major radius (a) and length (L) of the tubes that describes a similar transition from Euler buckling to fracture.

Using mechanical property data reported for 75-nm-thick ALD alumina, \(E = 164 \text{ GPa}\), \(\sigma_{fs} = 1.57 \text{ to } 2.56 \text{ GPa}\), \(v = 0.24 \text{ (27)}\), and Eqs. 1 and 2, the critical thickness-to-radius ratio that induces a transition from yielding to shell buckling in the nanolattices was calculated to be between \((t/a)_{\text{crit}} \approx 0.0361\) and 0.0262, and the critical radius-to-length ratio that denotes transition from yielding to Euler buckling was between \((a/L)_{\text{crit}} \approx 0.0391\) and 0.0755. The property space of all nanolattices studied here, along with their \(t/a\), \(a/L\), and predicted failure modes, are shown in table S1. The experimentally observed deformation behavior of each sample is also noted in the table.

The radius-to-length ratios, \(a/L\), for nanolattices studied here ranged from 0.0750 to 0.1800. All of these values are greater than or equal to \((a/L)_{\text{crit}}\) predicted by Eq. 2, which means that in an ideal structure, the beams will fracture before the Euler buckling condition is met. This prediction is consistent with our experimental results; no Euler buckling was observed in our in situ compression experiments (Fig. 2 and movies S1 to S3). This model is not capable of capturing local-scale stress concentrations, nor does it account for structures with a high degree of misalignment or pre-bending of the beams, which have been reported to reduce the critical load required to initiate buckling (6). The \(a/L\) values of the nanolattices are close to \((a/L)_{\text{crit}}\), suggesting that Euler buckling may occur in the samples with a large degree of misaligned or pre-bent beams, but it is not observed experimentally to be a dominant deformation mechanism.

The thickness-to-diameter ratios, \(t/a\), of the nanolattices ranged from 0.0059 to 0.0862, which overlaps the range of \((t/a)_{\text{crit}}\) predicted by Eq. 1. For thick-walled structures, whose \(t/a \geq 0.030\), \((t/a)_{\text{crit}}\), the model predicts that failure of the beams is dominated by brittle fracture within the alumina tubes. Fractured segments of tubes are unable to carry any load, so every failure event will cause a strain burst whose magnitude depends on the amount of strain energy stored in the system before failure. These predictions are corroborated by experimental stress-strain data for the thick-walled structures (Figs. 2, I and J, and 3, E and F, and movie S3).

Failure in the thin-walled structures, whose \(t/a \leq (t/a)_{\text{crit}} \leq 0.020\), is predicted to occur primarily via shell buckling, which is an elastic failure mode. This type of failure corresponds to a plateau in the stress-strain data caused by a gradual drop in load-carrying capacity of the beams (29), in contrast to the immediate drop in load-carrying capacity associated with fracture. Bending of an isolated thin-walled hollow beam often leads to shell buckling bifurcation, which can cause a jump in displacement (29).

In a truss structure, the interactions and nodal support among all the beams delay the onset of bifurcation and allow the beams to gradually settle into a new mode. Shell buckling in thin-walled nanolattices is manifested as wrinkling.

![Fig. 3. Mechanical tests on varying wall thickness and relative density samples. (A to D) Stress-strain plots of structures with varying wall thicknesses showing the transition from brittle to ductile-like deformation in thinner-walled structures. (E to J) Post-compression images of the nanolattices showing the recoverability as wall thickness is reduced.](image-url)
The proposed shell buckling model does not take into account the microstructural or material details, nor is it capable of predicting the deformation of structures in the transition regime of $0.020 \leq t/a \leq 0.030$. It is helpful in qualitatively explaining deformation in this regime, where nanolattices experience a complex stress state with compressive, tensile, and shear components. Fracture occurs primarily under tension, and shear and buckling occur only in compression, which means that the stress state within the beams can simultaneously satisfy fracture and buckling conditions. This is observed experimentally as a mixing of fracture and buckling failure modes, along with suppressed strain burst behavior and some recoverability (Fig. 3, G and I, and movie S2).

Elastic recovery has been studied previously in metallic and polymer lattices, and models have been proposed for their recoverability (21, 30–32). None of these works account for the observed ductile-like behavior of the ceramic nanolattices, and elastically deformable structures composed of intrinsically brittle materials such as ceramics are virtually unexplored. We postulate that reducing the $t/a$ ratio to below $(t/a)_{\text{ren}}$ derived in Eq. 1 enables failure via shell buckling, an elastic failure mode that causes minimal damage to the beams and nodes and allows the structure to recover. The transition to elastic failure is a necessary condition to prevent initial yielding or fracture of the constituent material but not a sufficient condition to ensure recovery of the structure. Figure 2D shows that during shell buckling, the global deformation is accompanied by localized wrinkling and warping of the tube walls. This results in confined regions of high stress that can subsequently lead to localized fracture (Figs. 2E and 3I). The propagation of these localized microcracks depends on the overall stress landscape and flaw distribution. If a crack extends into a region of high tensile stresses, or if numerous flaws reside near a crack tip, it is likely to propagate through the node and can potentially result in fracture of the tube. If an existing crack extends into a region of compressive stress, or if the stress field is insufficient to continue the crack extension, its propagation will be suppressed so that the tubes may never fully fracture. In this mechanism, a sufficient number of nodal connections remain intact to enable the structure to recover nearly fully to its original shape. The applied compressive load reduces the local tensile stresses within the tube walls that are generated by bending of the beams, which generates a compressive stress state at the nodes that can impede the propagation of a crack. As the $t/a$ is reduced, shell buckling will commence at a lower applied load (Eq. 1), which lowers the probability of initiating and/or propagating an existing crack. The wall thicknesses of alumina are on the order of tens of nanometers, a length scale that has been shown to exhibit enhanced strengths and damage tolerance caused by a statistically lower probability of finding a weak defect (1). These are some of the phenomena that collectively give rise to recoverability of the alumina nanolattices (Figs. 2E and 3H and figs. S3 and S4).

We discovered that the strength and Young’s modulus of all our octet-truss nanolattices follow a power law scaling with relative density as $\sigma_{\text{n}} \sim \rho^{1.76}$ and $E \sim \rho^{1.63}$ (Fig. 4, A and B). This scaling outperforms traditional lightweight and ultralight bending-dominated structural materials, whose properties scale as $E \sim \rho^2$ or $E \sim \rho^{3/2}$ (21), but does not follow the analytic prediction for an ideal stretching-dominated structure, $\sigma_{\text{n}} \sim \rho$ and $E \sim \rho^{5/2}$. Such a deviation from the analytic prediction can be explained, in part, by factors such as the ellipticity of the tubes, structural imperfections, and non-idealities of the experimental setup. We attribute this deviation primarily to the hollowness of the tubes, which affects the structural integrity of the nodes, where the highest stress concentrations will occur (30, 31).

The strength and deformation of an ideal, monolithic, stretching-dominated cellular solid is governed by stretching of the beams, with the nodes acting as rigid pin-jointed elements that perfectly transfer load between truss members.

![Fig. 4. Strength and stiffness versus density of alumina nanolattices. (A and B) Stiffness and strength plotted against relative density for all tested samples. Data clearly obey a power law, with little deviation across wall thicknesses and failure modes. (C and D) Material property plots (Materials Property CES Selector software by Granta Design) of the experimental stiffness and strength data against density for existing materials, showing that the materials created in this work reach a new niche in the high-strength and stiffness lightweight material parameter space.](image-url)
The electrolysis of water using renewable energy inputs is being actively pursued as a route to sustainable hydrogen production. Here we introduce a recyclable redox mediator (silicotungstic acid) that enables the coupling of low-pressure production of oxygen via water oxidation to a separate, catalytic hydrogen production step outside the electrolyzer that requires no post-electrolysis energy input. This approach sidesteps the production of high-pressure gases inside the electrolytic cell (a major cause of membrane degradation) and essentially eliminates the hazardous issue of product gas crossover at the low current densities that characterize renewables-driven water-splitting devices. We demonstrated that a platinum-catalyzed system can produce pure hydrogen over 30 times faster than state-of-the-art proton exchange membrane electrolysers at equivalent platinum loading.

**WATER SPLITTING**

Decoupled catalytic hydrogen evolution from a molecular metal oxide redox mediator in water splitting

Benjamin Rausch, Mark D. Symes, Greig Chisholm, Leroy Cronin*  

The electrolysis of water using renewable energy inputs is being actively pursued as a route to sustainable hydrogen production. Here we introduce a recyclable redox mediator (silicotungstic acid) that enables the coupling of low-pressure production of oxygen via water oxidation to a separate, catalytic hydrogen production step outside the electrolyzer that requires no post-electrolysis energy input. This approach sidesteps the production of high-pressure gases inside the electrolytic cell (a major cause of membrane degradation) and essentially eliminates the hazardous issue of product gas crossover at the low current densities that characterize renewables-driven water-splitting devices. We demonstrated that a platinum-catalyzed system can produce pure hydrogen over 30 times faster than state-of-the-art proton exchange membrane electrolysers at equivalent platinum loading.

**REFERENCES AND NOTES**

23. See the supplementary materials.

**SUPPLEMENTARY MATERIALS**

www.sciencemag.org/content/345/6202/1322/suppl/DC1  
Materials and Methods: Figs. S1 to S6  
Table S1  
Reference (33)  
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