MATERIALS SCIENCE

Ultrastrong colloidal crystal metamaterials engineered with DNA

Yuanwei Li^{1,2+}, Hanxun Jin^{2,3+}, Wenjie Zhou^{2,4}, Zhe Wang^{2,4}, Zhaowen Lin^{2,3}, Chad A. Mirkin^{1,2,4}*, Horacio D. Espinosa^{2,3}*

Lattice-based constructs, often made by additive manufacturing, are attractive for many applications. Typically, such constructs are made from microscale or larger elements; however, smaller nanoscale components can lead to more unusual properties, including greater strength, lighter weight, and unprecedented resiliencies. Here, solid and hollow nanoparticles (nanoframes and nanocages; frame size: ~15 nanometers) were assembled into colloidal crystals using DNA, and their mechanical strengths were studied. Nanosolid, nanocage, and nanoframe lattices with identical crystal symmetries exhibit markedly different specific stiffnesses and strengths. Unexpectedly, the nanoframe lattice is approximately six times stronger than the nanosolid lattice. Nanomechanical experiments, electron microscopy, and finite element analysis show that this property results from the buckling, densification, and size-dependent strain hardening of nanoframe lattices. Last, these unusual open architectures show that lattices with structural elements as small as 15 nanometers can retain a high degree of strength, and as such, they represent target components for making and exploring a variety of miniaturized devices.

INTRODUCTION

Engineering material architecture at the nanoscale is a powerful way of generating structures with unusual chemical and physical properties that cannot be found with their bulk counterparts (1). Nanostructured metamaterials, in particular, are promising for a wide range of applications in the semiconductor, aerospace, automotive, and biomedical industries (2–4). For example, lattices made from metals, ceramics, or polymers with nano- and micrometer dimensions can be used as light traps (5) and reversible energy absorbers (6), and can exhibit ultralow thermal conductivity (7), ultralow densities (lightweight) (8), high degrees of recoverability (9), and enhanced mechanical strengths and stiffnesses (10, 11).

The properties of mechanical metamaterials derive from their architecture rather than solely from the composition of the constituent components (12-14). Because most mechanical metamaterials are fabricated from top-down lithographic procedures (e.g., additive manufacturing and interference lithography) (15, 16), it is difficult to make them at scale (17, 18). Moreover, these strategies typically yield polycrystalline structures with limited spatial resolution (typical unit cell size > 500 nm) (19, 20). It is remarkably challenging to prepare architected lattices with unit cells below this size regime (i.e., <500 nm), leaving the mechanical properties of such lattices largely unexplored. Overcoming these challenges would enable new spatial control in material synthesis and, therefore, the development of new metamaterials with mechanical properties that combine both architecture design and nanoscale size effects.

Here, metallic lattices (unit cell: ~100 nm, frame size: ~15 nm) were prepared using colloidal crystal engineering with DNA (21, 22). Specifically, DNA-functionalized solid and hollow

nanoparticles were used as model systems to study the structuremechanical property relationships of this new class of materials. The topologies and densities of these lattices are highly tailorable and can be controlled by changing the shapes and dimensions of the lattice building blocks. This type of control, in principle, offers a way of systematically studying and realizing metamaterials with unusual mechanical properties. By combining in situ micromechanical measurements, electron microscopy, and finite element analysis (FEA), we systematically investigated and compared the mechanical properties of a series of simple cubic lattices assembled from metallic nanoframes (NFs), nanocages (NCs), and nanosolids (NSs) with varying densities and porosities. In situ mechanical compression results reveal that NF lattices have the highest specific stiffness (~550 MPa/g cm⁻³) and specific strength (~125 MPa/g cm⁻³) compared to NC and NS lattices, which can be attributed to the lower density and smaller NF feature size (frame thickness: ~15 nm). NF lattices are structurally robust, even after compression, because of their low volume fractions, large unit cell compressibility, and strain hardening. Because of the material generality of colloidal crystal engineering with DNA and the vast number of structural entities possible (22, 23), these observations provide a foundational testbed for preparing a wide variety of mechanical metamaterials that may be important in miniaturized electronics, robotics, aerospace, automotive, and medical devices.

RESULTS

Truncated cubic NSs, NFs, and NCs were synthesized through seedmediated growth (22, 24) and used as building blocks to prepare the targeted lattices. Three types of lattices, with different densities and porosities, were constructed through the DNA-mediated assembly of these nanoparticles, including Au NSs, Pt-Au core-shell NCs, and Pt-Au core-shell NFs (Figs. 1 and 2 and figs. S1 and S2). Assembly into simple cubic lattices was achieved through the design of particle-DNA constructs (summarized in table S1) that favor edge-to-edge (for NFs) or facet-to-facet (for NCs and NSs)



Copyright © 2023 True Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. No claim to original U.S. Government Works. Distributed under a Creative Commons Attribution NonCommercial License 4.0 (CC BY-NC).

¹Department of Chemical and Biological Engineering, Northwestern University, Evanston, IL 60208, USA. ²International Institute for Nanotechnology, Northwestern University, Evanston, IL 60208, USA. ³Department of Mechanical Engineering, Northwestern University, Evanston, IL 60208, USA. ⁴Department of Chemistry, Northwestern University, Evanston, IL 60208, USA.

^{*}Corresponding author. Email: chadnano@northwestern.edu (C.A.M.); espinosa@ northwestern.edu (H.D.E.)

⁺These authors contributed equally to this work.



Fig. 1. Schematic of 3D-printed and DNA assembled lattices. (**A**) Schematic showing overall size of a typical metallic structure made from additive manufacturing (left, building block size: >1000 nm) compared to the lattices in this work (right, building block size: ~100 nm, NF thickness: ~15 nm). (**B**) Schematic showing the simple cubic structure assembled from truncated cubic NFs (building block size: ~100 nm). (**C**) Schematic showing the DNA connections between building blocks.

interactions (22). After assembly, these lattices were stabilized with Ag⁺ (25), before structural and mechanical analysis under a tilted scanning electron microscope. Before this work, metal lattices have been traditionally prepared using additive manufacturing processes that can only yield lattice structures with unit cell sizes of >500 nm (Fig. 1A) (16). In contrast, lattices synthesized from this bottom-up assembly strategy provide access to structures with ~100-nm unit cells and feature sizes as small as ~15 nm (frame thickness; Figs. 1, B and C, and 2). As evident from the scanning electron microscopy (SEM) images, all three lattice types exhibit well-defined cubic habits (Fig. 2, A, B, D, E, G, and H) with relatively smooth surfaces that make them well suited for mechanical measurements.

To quantify the mechanical properties of these lattices, we performed uniaxial in situ microcompression experiments with a miniaturized compression platform inside a SEM chamber (see Materials and Methods for details). For each lattice type, the Young's modulus, ultimate compressive strength, density, specific stiffness, and specific compressive strength were measured and summarized in tables S2 and S3. The deformation states and stress-strain behaviors are shown in Fig. 3 (A, C, and E) and Fig. 3 (B, D, and F), respectively. We found that after an initial linear elastic behavior, nonlinearities, arising from plasticity and damage in the form of multiple microcracks, initiate and propagate when the compressive strain is larger than 10% for the NS (Fig. 3A and movie S1) and NC lattices (Fig. 3C and movie S2). In the case of the NS and NC lattices, microcracks develop upon breakage of DNA bonds between adjacent lattices rather than the failure of lattice members, as observed in the titled SEM images after compression (Fig. 2, C and F) and confirmed by finite element modeling (FEM)

Li et al., Sci. Adv. 9, eadj8103 (2023) 29 September 2023

(vide infra). As a result of damage propagation and microcrack coalescence, a progressive decrease in compressive stress is observed followed by stress hardening due to densification of the structures (Fig. 3, B and D). Furthermore, microcracks may spontaneously form due to local defects within the crystals. As a result, their mechanical responses after linear elasticity (when the curve is nonlinear) can vary among different crystals (Fig. 3, B and D). The NF lattices did not exhibit strain softening but rather hardening up to a compressive strain of 40% (Fig. 3E and movie S3). SEM images after compression (Fig. 2I) show very limited and localized surface cracking, with the crystals maintaining their overall structural integrity. Consequently, the stress-strain response for NF lattices is observed to be continuous (Fig. 3F), and the ultimate stress reaches 386.95 ± 3.04 MPa, which is more than 1.5 times higher than that of the NS lattices. We found that Young's modulus of the NF lattice is comparable to the NC lattice; however, the density of the NF lattice is more than two times smaller than that of the NC lattice (tables S2 and S3). We also found that none of these three structures fully recovered after unloading.

Figure 3 (G and H) shows the specific stiffness and strength of all three structures, i.e., Young's modulus and ultimate strength normalized by their density. We found that the specific stiffness of the NF is approximately two times greater than that of the NC and the NS lattices. Notably, the specific strength of the NF lattice shows about six times improvement when compared to NC and NS lattices because of their relatively low density and overall structural integrity (table S3). It is worth noting that the three lattices were synthesized using the same DNA-mediated assembly technique with a similar unit cell size (~100 nm). Therefore, we hypothesize that the unprecedented mechanical behavior of the NF lattice can be attributed to the lattice architectural design and nanoscale size effects of the metallic constituents.

To gain insight into the deformation mechanisms of these three lattices and to decouple the role between architectural design and material size effects, we performed finite element (FE) simulations of the uniaxial compression on the three structures composed of 12 \times 12 \times 6 unit cells (see Materials and Methods for details). The simulation included a reasonably large number of unit cells, with the same geometry and dimensions as the experimental materials. In the experimental samples, we observed that the crystals have defects in the form of random vacancies or steps on the surfaces (Fig. 2, B, E, and H). Moreover, the building blocks in the metallic lattices exhibited small size variations in their dimensions (fig. S1). These imperfections could control the onset of plasticity and microcracking; however, for simplicity and to capture average effects as measured in the experiments, the FE model reported here used perfect crystals with uniform unit cell dimensions bonded by DNA layers. The metallic constituents are modeled with an elastoplastic constitutive law, and the DNA, at interfaces between cells, is modeled to exhibit elastoplastic behavior with superposition of ductile damage only in tension. The simulated stress-strain curves for the three lattices are shown in Fig. 3 (B, D, and F). Model parameters were identified from the measured stress-strain curves. We found good agreement between FE modeling and experimental results except for very large strains, specifically more than 30%, which can be attributed in part to the finite domain size used in the simulations. The color contours depict the equivalent plastic strain (defined as PEEQ in ABAQUS) plotted in the range between 0.0 and 0.8, and Fig. 4 (A to C) depicts the simulated

SCIENCE ADVANCES | RESEARCH ARTICLE



Fig. 2. Simple cubic lattices with different densities. (A and B) Model (A) and the corresponding SEM images with different magnifications (B) of simple cubic lattices assembled from truncated cubic NSs. (C) SEM images showing the structural deformation of NS lattices after compression. (D and E) Model (D) and the corresponding SEM images with different magnifications (E) of simple cubic lattices assembled from truncated cubic NCs. (F) SEM images showing the structural deformation of NC lattices after compression. (G and H) Model (G) and the corresponding SEM images with different magnifications (H) of simple cubic lattices assembled from truncated cubic NCs. (F) SEM images showing the structural deformation of NC lattices after compression. (G and H) Model (G) and the corresponding SEM images with different magnifications (H) of simple cubic lattices assembled from truncated cubic NFs. (I) SEM images showing the structural deformation of NF lattices after compression. The edge length of the building blocks is ~100 nm. Scale bars, 1 µm.

crystal morphology and cross-sectional views of the three lattices, revealing concentrations of plastic strain. From the simulated deformations (see FEM supplementary movies), we infer plasticity and multicrack propagation during the compression of the NS (Fig. 4A) and NC (Fig. 4B) lattices. By contrast, the NF lattices retain the overall structural integrity via plastic deformation and lattice buckling. We found that building blocks at the bottom of the NF and NC lattices severely buckle, which is consistent with the experimental observations (fig. S9). Furthermore, the cross-sectional view of the NF lattices (Fig. 4C) shows that the building blocks near the center buckle and collapse more severely than in the NC lattices. These progressive buckling and densification processes explain the stress hardening observed in the stress-strain curves. It also shows that the NF lattices can absorb notable strain energy during compression, which potentially prevents the early breakage of the DNA bonding and maintains the overall structural integrity of NF lattices.

Upon compression using a small strain (2.5%), the NF metallic lattices absorb more than 50% of the total strain energy, while the NS motif absorbs <3% of the total strain energy (Fig. 4D). As strain increases, NF lattices continue absorbing more strain energy than NS and NC lattices because of the buckling of NF unit cells. These results suggest that by tailoring the architecture with different instability mechanisms, one could fabricate assembled mechanical metamaterials with higher deformation tolerance and increased load-carrying capacity.

Another significant contribution to the superior mechanical properties of NF lattices is the strong strain hardening experienced by the metallic building blocks in the lattices. To match the continuous hardening of NF lattices, as observed from experiments (Fig. 3F), we found that an elastoplastic constitutive law with substantial strain hardening (Eq. 1) is needed

$$\sigma = \sigma_{\rm y}^0 + H\overline{\epsilon}_{\rm p} \tag{1}$$

Here, σ_v^0 is the yield stress, H is the hardening coefficient, and $\overline{\epsilon}_p$ is the equivalent plastic strain. Figure 4E plots the simulated stressstrain curves for NF lattices with H ranging from 0 to 15 GPa. As expected, *H* has a significant effect on the mechanical properties beyond yielding. We found that H = 15 GPa provides the best fit for the NF metallic lattices. However, for NC and NS lattices, we found that an elastic perfectly plastic model (i.e., =0) is needed to match the experimental results. To understand this difference, we conducted high-resolution transmission electron microscopy (TEM) to study the lattice constituents. The NSs are 100% singlecrystalline Au with an edge length of ~90 nm (26), while NCs and NFs have Pt cores coated with ~5-nm single-crystalline Au (fig. S2). The Pt cores consist of fused nanoparticles with ~2 to 5 nm diameters. Compared to NCs with an edge length of ~110 nm, NFs have a smaller feature size (frame size: 15 nm). We highlight that the feature size difference results in a smaller-is-stronger nanoscale size effect exhibited by NF lattices. Our previous in situ TEM investigation of penta-twinned silver nanowire tensile experiments (27) showed that yield stress and strain hardening significantly increase when the nanowire diameter reduces to ~40 nm ($H \sim 17.8$ GPa). Likewise, recent experiments conducted with [110] Au singlecrystal nanowires (28), ~60 nm in diameter, reveal a room temperature behavior consistent with the high strain hardening rate identified in the NF lattices. Molecular dynamics simulations (29) have shown that this size-dependent strain hardening effect is due to the preexisting defects, which serve as obstacles for dislocation motion.



Fig. 3. In situ SEM microcompression experiments on three lattices. (A to F) SEM images during compression and stress-strain curves for (A and B) NS lattices, (C and D) NC lattices, and (E and F) NF lattices. (G) Specific stiffness for the three lattices. (H) Specific strength for the three lattices. The red curves in (B), (D), and (F) are FEAsimulated curves. The open circle markers in (B), (D), and (F) indicate the ultimate stress. Scale bars, 5 µm (A and C) and 2 µm (E). E: strain. The SEM images for (A) correspond to Samp2 in (B); (C) corresponds to Samp3 in (D); (E) corresponds to Samp2 in (F).

As the NF truss diameter reduces to ~15 nm, the dense packing of Pt nanoparticles reduces the effective grain size and the distance between dislocation sources and grain boundaries, which increases both yield stress and strain hardening. By reducing the feature size down to ~10 to 20 nm, full utilization of nanoscale size effects imparts these lattice metamaterials with superior mechanical properties.

To place the findings reported here in context, we plotted the specific strength of the NC and NF lattices on a log scale together with other mechanical metal metamaterials obtained from topdown additive manufacturing techniques (Fig. 5). While NF lattices have a specific strength of ~125 MPa/g cm⁻³ (table S3), which is similar to that of Ti-6Al-4V metallic lattices (30) fabricated at millimeter scales with traditional top-down additive manufacturing



Fig. 4. FEA simulations of uniaxial compression of three lattices. Simulated crystal morphologies and cross-sectional views for (A) NS lattices, (B) NC lattices, and (C) NF lattices after deformation. Color contours of equivalent plastic strain (PEEQ) in the range between 0.0 and 0.8. (D) Strain energy density ratio, at four compressive strains, between the strain energy in the building blocks of the metallic lattices and the total strain energy of the system. (E) Simulated stress-strain curves, for different hardening coefficient *H*, for the case of NF lattices.

processes, our data represent the largest lattice miniaturization to date without degradation of specific strength. Other attempts to miniaturize NF lattices, for example, the architected nickel nanolattices with a frame size of 300 to 400 nm (16), exhibit a much lower specific strength of ~3 to 10 MPa/g cm⁻³. From these observations, it is clear that mechanical metamaterials made via colloidal crystal engineering with DNA can exhibit reduced sensitivity to imperfections and unprecedented high specific strengths.

DISCUSSION

This work is important for the following reasons: (i) It provides a new and general method for preparing three-dimensional mechanical metamaterials spanning a wide variety of building blocks and crystal parameters that go beyond the proof-of-concept structures reported herein; hence, it is a major step toward materials by design enabled by colloidal crystal engineering with DNA, and (ii) it demonstrates that colloidal superlattices containing metallic features as small as 15 nm can maintain a remarkable level of strength. The mechanical characteristics of these lattices result from a combination of their plasticity, feature sizes, and architectural designs. In this regard, it is worth noting that the high strength of



Fig. 5. Specific strength–frame size plot showing properties of lattices compared to other reported metal lattices. These include Ti-6Al-4V-1 made by electron beam melting (*30*), Ti-6Al-4V-2 made by selective laser melting (*36*), AlSi₁₀Mg (*37*), stainless steel 316L (*38*), silver (*39*), NiTi (*40*), copper (*41*), and nickel (*16*).

NF lattices originates from the strong size-dependent strain hardening exhibited by metallic members and deformation mechanisms (buckling and densification). The high ductility of NF lattices arises from the unit cell compressibility, which helps absorb strain energy while maintaining the overall structural integrity. This work is a step beyond the classical approaches to designing and synthesizing architected materials on the nanometer scale, providing a route to unexplored structural precision that will be essential for broadening the scope of functional mechanical metamaterials accessible and therefore the fundamental studies that can be carried out on such structures.

MATERIALS AND METHODS

Materials

Ascorbic acid (99%), cetyltrimethylammonium bromide (99%), hydrogen tetrachloroaurate(III) (99.9+%), hydrogen hexachloroplatinate(IV) hydrate (99%), sodium chloride (NaCl, 99.5%), trisodium citrate dihydrate (sodium citrate, 99.9%), hydrochloric acid, silver nitrate (99.9999%), sodium borohydride (99.99%), cetylpyridinium chloride (99+%), sodium dodecyl sulfate (SDS) (99+%), dithiothreitol (DTT) (95%), and sodium iodide (99%) were purchased from Millipore Sigma. Oligonucleotide synthesis reagents were obtained from Glen Research. All chemicals were used as purchased without further purification.

Synthesis of NSs, NFs, and NCs

Truncated cubic gold nanoparticles were synthesized following published protocols (24, 26). In this strategy, iterative oxidative dissolution and reductive growth reactions were used to control nanoparticle seed structural uniformity. Subsequently, these seeds were used to template the growth of cubes, and then cubes were used as seeds for the growth of truncated cubic NSs. Truncated cubic NFs and NCs were synthesized based on previously published methods (22), which includes three chemical reactions: (i) edge-selective or facet-selective growth of Pt on truncated cubes, (ii) selective etching of Au, and (iii) overgrowth of Au on Pt skeletons to form Pt-Au NFs or NCs.

DNA synthesis and purification

Oligonucleotide sequences were designed before synthesis (table S1). Oligonucleotides were synthesized on a Mermade 12 DNA synthesizer. After synthesis, the oligonucleotides were cleaved from the controlled pore glass beads using a solution containing a 1:1 volume mixture of 30% ammonium hydroxide and 40% aqueous methylamine solution (incubation at 55°C for 30 min). After evaporation of the ammonium hydroxide and methylamine, oligonucleotides were purified using reverse-phase high-performance liquid chromatography on a Microsorb C18 column (10 μ m, 300 × 10 mm). The oligonucleotides were treated with acetic acid solution and ethyl acetate solutions to remove the 4,4'-dimethoxytrityl functional groups. After synthesis and purification, all oligonucleotides were characterized by matrix-assisted laser desorption ionization time-of-flight mass spectrometry to confirm their molecular mass and purity.

Assembly and stabilization of lattices with different densities

All of the synthesized nanoparticles, including NSs, NFs, and NCs, were functionalized with anchor DNA following a literature procedure (31, 32). First, 3'-propylthiol-terminated anchor strands were incubated with 100 mM DTT for 1 hour to cleave the disulfide end. The DTT was removed via size exclusion chromatography with a NAP25 column (GE Healthcare). Later, the anchor strands were added to the nanoparticle suspensions (~8 nmol DNA per ml of nanoparticles), and 1 wt % SDS and 1 M sodium phosphate (pH 7.5) were added to reach final concentrations of 0.01 wt % SDS and 10 mM sodium phosphate, respectively. Next, stepwise additions of 5 M NaCl solution (with each aliquot raising the total NaCl concentration by approximately 0.1 M) were added to the solution until it reached a final concentration of 0.5 M NaCl; each addition was followed by 30 s of sonication. This solution was shaken overnight to maximize DNA loading. Excess DNA strands were removed by three rounds of centrifugation/supernatant removal/resuspension. After the final centrifugation step, the anchor-coated nanoparticles were redispersed in 0.5 M NaCl buffer (with 0.01 wt % SDS and 10 mM sodium phosphate buffer). Then, 10 nmol of DNA linkers was added to 200 µl of nanoparticle solution. Crystallization was performed through slow-cool annealing with a ProFlex polymerase chain reaction system (Applied Biosystems). Specifically, the temperature was slowly decreased from 65° to 25°C at a rate of 0.01°C/min. These crystals were stabilized with Ag⁺, which allows the transfer of lattices in the assembled state and preserves crystal symmetry for imaging and mechanical measurements using tilted SEM (25).

Nanomechanical experiments

Uniaxial in situ SEM microcompression experiments were performed using the set up reported (33, 34). The displacement field was set by a programmable piezo actuator with a diamond flat punch (50 mm diameter) and a resolution of 1 nm. The punch speed was set to achieve a quasi-static strain rate of $5 \times 10^{-3} \text{ s}^{-1}$. The load was measured by a load cell with a 1-N capacity and 4mN resolution. The displacement profile was corrected in accordance with the instrumentation and substrate compliance. The engineering stress-strain profiles were converted from corrected load-displacement profiles by normalizing the samples' footprint area and height, respectively. Young's modulus was defined by the slope of the linear stress-strain region. The ultimate stress was defined as the maximum stress before failure. We performed three experiments for NS and NC lattices and two experiments for NF lattices and found stress-strain data for all three structures to be reproducible.

FE modeling

The FE simulations were performed using the commercial software ABAQUS/Explicit 2021. To simulate the deformation process under the quasi-static loading condition, we ensured the kinetic energy to be negligible compared to the internal energy (fig. S4). The unit cell dimensions for the three lattices were determined from SEM images (see fig. S1). The DNA thickness t_{DNA} was calculated to be about 10 nm (35). We chose a specimen dimension ratio, between width/length and height, of 2:1, which is consistent with the actual crystal asperity ratio. We found that the number of unit cells has a negligible effect on the mechanical response when the strain is small but affects the response at larger strains due to boundary effects (fig. S6). Therefore, based on the domain size-dependent convergent tests reported in fig. S6 and the computational cost, we chose a simulation domain consisting of $12 \times 12 \times 6$ unit cells. The crystal domain was placed between a rigid substrate and a rigid flat punch, both modeled as analytical rigid surfaces (fig. S5). The substrate was fixed, and a displacement profile was set to the flat punch to compress the crystal until a compressive strain of $\varepsilon = 0.4$ was reached. The contact interaction was defined as "hard contact," and a friction penalty of $\mu = 0.2$ was used. The crystal domains were meshed into approximately 5 million quadratic tetrahedral elements (element type: C3D10). A typical mesh geometry for the NS is shown in fig. S7. Mesh sensitivity was checked to ensure that all reported solutions are converged solutions. The metallic members were modeled using an elastoplastic material constitutive law. The Young's modulus E, Poisson's ratio v, and density p were chosen to be 4 GPa, 0.415, and 19,000 kg/m³, respectively. The NS and NC lattices were modeled with a perfect elastoplastic model with yield stress $\sigma_v = 500$ MPa. The NF lattices were modeled with a linear isotropic hardening law

$$\sigma = \sigma_{\rm y}^0 + H\overline{\epsilon}_{\rm p}$$

with an initial yield stress $\sigma_y^0 = 750$ MPa and a hardening coefficient H = 15 GPa. In this equation, $\overline{\epsilon}_p$ is the equivalent plastic strain. From postmortem SEM observation, we concluded that fracture of metallic members was not present. Therefore, damage to metallic frames was not included. DNA was modeled as an elastoplastic material with a perfect plastic response, Young's modulus: $E_{\text{DNA}} = 200$ MPa, Poisson's ratio v = 0.4, and yield stress $\sigma_y^{\text{DNA}} = 100$ MPa. The density ρ was calculated as 560 kg/m³ (table S4). Failure of the DNA under tension was modeled using a linear damage evolution model with the equivalent plastic strain at failure initiation, $\overline{\epsilon}_0^T = 0.4$, and plastic displacement at full degradation, $\overline{u}_f^T = 1$ nm (fig. S8). Here

$$\overline{u}_{\rm f}^T = (\overline{\varepsilon}_{\rm f}^T - \overline{\varepsilon}_{\rm 0}^T) \cdot L$$

where $\overline{\mathbf{e}}_{f}^{T}$ is the equivalent plastic strain at full degradation and *L* is

the characteristic length for the DNA FE elements (L = 5 nm). The elements after full degradation were deleted during the simulation. We first identified the Young's modulus of DNA using a unit cell model subjected to periodical boundary conditions. Other simulation parameters were then iteratively determined to match the experimental stress-strain curves. Simulation parameters are listed in tables S4 to S6.

Supplementary Materials

This PDF file includes: Figs. S1 to S9 Tables S1 to S6 Legends for movies S1 to S9

Other Supplementary Material for this

manuscript includes the following: Movies S1 to S9

REFERENCES AND NOTES

- X. Xia, C. M. Spadaccini, J. R. Greer, Responsive materials architected in space and time. *Nat. Rev. Mater.* 7, 683–701 (2022).
- N. I. Zheludev, E. Plum, Reconfigurable nanomechanical photonic metamaterials. *Nat. Nanotechnol.* 11, 16–22 (2016).
- J.-H. Lee, J. P. Singer, E. L. Thomas, Micro-/nanostructured mechanical metamaterials. Adv. Mater. 24, 4782–4810 (2012).
- M. Kadic, G. W. Milton, M. van Hecke, M. Wegener, 3D metamaterials. Nat. Rev. Phys. 1, 198–210 (2019).
- C. Fei Guo, T. Sun, F. Cao, Q. Liu, Z. Ren, Metallic nanostructures for light trapping in energyharvesting devices. *Light Sci. Appl.* 3, –e161 (2014).
- T. Frenzel, C. Findeisen, M. Kadic, P. Gumbsch, M. Wegener, Tailored buckling microlattices as reusable light-weight shock absorbers. *Adv. Mater.* 28, 5865–5870 (2016).
- N. G. Dou, R. A. Jagt, C. M. Portela, J. R. Greer, A. J. Minnich, Ultralow thermal conductivity and mechanical resilience of architected nanolattices. *Nano Lett.* 18, 4755–4761 (2018).
- T. A. Schaedler, A. J. Jacobsen, A. Torrents, A. E. Sorensen, J. Lian, J. R. Greer, L. Valdevit, W. B. Carter, Ultralight metallic microlattices. *Science* 334, 962–965 (2011).
- L. R. Meza, S. Das, J. R. Greer, Strong, lightweight, and recoverable three-dimensional ceramic nanolattices. *Science* 345, 1322–1326 (2014).
- X. Zheng, H. Lee, T. H. Weisgraber, M. Shusteff, J. DeOtte, E. B. Duoss, J. D. Kuntz, M. M. Biener, Q. Ge, J. A. Jackson, S. O. Kucheyev, N. X. Fang, C. M. Spadaccini, Ultralight, ultrastiff mechanical metamaterials. *Science* **344**, 1373–1377 (2014).
- 11. J. Bauer, A. Schroer, R. Schwaiger, O. Kraft, Approaching theoretical strength in glassy carbon nanolattices. *Nat. Mater.* **15**, 438–443 (2016).
- J. Qi, Z. Chen, P. Jiang, W. Hu, Y. Wang, Z. Zhao, X. Cao, S. Zhang, R. Tao, Y. Li, D. Fang, Recent progress in active mechanical metamaterials and construction principles. *Adv. Sci.* 9, 2102662 (2022).
- J. Bauer, L. R. Meza, T. A. Schaedler, R. Schwaiger, X. Zheng, L. Valdevit, Nanolattices: An emerging class of mechanical metamaterials. *Adv. Mater.* 29, 1701850 (2017).
- K. Bertoldi, V. Vitelli, J. Christensen, M. van Hecke, Flexible mechanical metamaterials. Nat. Rev. Mater. 2, 17066 (2017).
- J. U. Surjadi, L. Gao, H. Du, X. Li, X. Xiong, N. X. Fang, Y. Lu, Mechanical metamaterials and their engineering applications. *Adv. Eng. Mater.* **21**, 1800864 (2019).
- A. Vyatskikh, S. Delalande, A. Kudo, X. Zhang, C. M. Portela, J. R. Greer, Additive manufacturing of 3D nano-architected metals. *Nat. Commun.* 9, 593 (2018).
- Q. Geng, D. Wang, P. Chen, S.-C. Chen, Ultrafast multi-focus 3-D nano-fabrication based on two-photon polymerization. *Nat. Commun.* **10**, 2179 (2019).
- 18. A. Stein, N. A. Mara, Nano goes the distance. *Nat. Mater.* **20**, 1456–1458 (2021).
- L. Hirt, A. Reiser, R. Spolenak, T. Zambelli, Additive manufacturing of metal structures at the micrometer scale. *Adv. Mater.* 29, 1604211 (2017).
- M. Vaezi, H. Seitz, S. Yang, A review on 3D micro-additive manufacturing technologies. *Int. J. Adv. Manuf. Technol.* 67, 1721–1754 (2013).
- C. A. Mirkin, R. L. Letsinger, R. C. Mucic, J. J. Storhoff, A DNA-based method for rationally assembling nanoparticles into macroscopic materials. *Nature* 382, 607–609 (1996).

- Y. Li, W. Zhou, I. Tanriover, W. Hadibrata, B. E. Partridge, H. Lin, X. Hu, B. Lee, J. Liu, V. P. Dravid, K. Aydin, C. A. Mirkin, Open-channel metal particle superlattices. *Nature* **611**, 695–701 (2022).
- C. R. Laramy, M. N. O'Brien, C. A. Mirkin, Crystal engineering with DNA. Nat. Rev. Mater. 4, 201–224 (2019).
- Y. Li, H. Lin, W. Zhou, L. Sun, D. Samanta, C. A. Mirkin, Corner-, edge-, and facet-controlled growth of nanocrystals. *Sci. Adv.* 7, eabf1410 (2021).
- T. Oh, S. S. Park, C. A. Mirkin, Stabilization of colloidal crystals engineered with DNA. Adv. Mater. 31, e1805480 (2019).
- M. N. O'Brien, M. R. Jones, K. A. Brown, C. A. Mirkin, Universal noble metal nanoparticle seeds realized through iterative reductive growth and oxidative dissolution reactions. *J. Am. Chem. Soc.* **136**, 7603–7606 (2014).
- R. A. Bernal, A. Aghaei, S. Lee, S. Ryu, K. Sohn, J. Huang, W. Cai, H. Espinosa, Intrinsic bauschinger effect and recoverable plasticity in pentatwinned silver nanowires tested in tension. *Nano Lett.* **15**, 139–146 (2015).
- 28. Z. Lin, thesis, Northwestern University, Evanston, IL, (2022).
- S. Narayanan, G. Cheng, Z. Zeng, Y. Zhu, T. Zhu, Strain hardening and size effect in five-fold twinned Ag nanowires. *Nano Lett.* 15, 4037–4044 (2015).
- E. Hernández-Nava, C. J. Smith, F. Derguti, S. Tammas-Williams, F. Leonard, P. J. Withers, I. Todd, R. Goodall, The effect of defects on the mechanical response of Ti-6Al-4V cubic lattice structures fabricated by electron beam melting. *Acta Mater.* **108**, 279–292 (2016).
- E. Auyeung, T. I. N. G. Li, A. J. Senesi, A. L. Schmucker, B. C. Pals, M. O. de la Cruz, C. A. Mirkin, DNA-mediated nanoparticle crystallization into Wulff polyhedra. *Nature* 505, 73–77 (2014).
- L. Sun, H. Lin, Y. Li, W. Zhou, J. S. Du, C. A. Mirkin, Position- and orientation-controlled growth of wulff-shaped colloidal crystals engineered with DNA. *Adv. Mater.* 32, 2005316 (2020).
- Z. Lin, D. J. Magagnosc, J. Wen, C.-S. Oh, S.-M. Kim, H. D. Espinosa, In situ SEM high strain rate testing of large diameter micropillars followed by TEM and EBSD postmortem analysis. *Exp. Mech.* **61**, 739–752 (2021).
- Z. Lin, L. S. Novelino, H. Wei, N. A. Alderete, G. H. Paulino, H. D. Espinosa, S. Krishnaswamy, Folding at the Microscale: Enabling multifunctional 3D origami-architected metamaterials. *Small* 16, 2002229 (2020).
- Q.-Y. Lin, J. A. Mason, Z. Li, W. Zhou, M. N. O'Brien, K. A. Brown, M. R. Jones, S. Butun, B. Lee, V. P. Dravid, K. Aydin, C. A. Mirkin, Building superlattices from individual nanoparticles via template-confined DNA-mediated assembly. *Science* **359**, 669–672 (2018).
- V. J. Challis, X. Xu, L. C. Zhang, A. P. Roberts, J. F. Grotowski, T. B. Sercombe, High specific strength and stiffness structures produced using selective laser melting. *Mater. Des.* 63, 783–788 (2014).
- C. Yan, L. Hao, A. Hussein, S. L. Bubb, P. Young, D. Raymont, Evaluation of light-weight AlSi10Mg periodic cellular lattice structures fabricated via direct metal laser sintering. *J. Mater. Process. Technol.* **214**, 856–864 (2014).

- S. Tsopanos, R. A. W. Mines, S. McKown, Y. Shen, W. J. Cantwell, W. Brooks, C. J. Sutcliffe, The influence of processing parameters on the mechanical properties of selectively laser melted stainless steel microlattice structures. J. Manuf. Sci. Eng. 132, 04101 (2010).
- M. S. Saleh, C. Hu, R. Panat, Three-dimensional microarchitected materials and devices using nanoparticle assembly by pointwise spatial printing. *Sci. Adv.* 3, e1601986 (2017).
- M. Speirs, B. Van Hooreweder, J. Van Humbeeck, J.-P. Kruth, Fatigue behaviour of NiTi shape memory alloy scaffolds produced by SLM, a unit cell design comparison. J. Mech. Behav. Biomed. Mater. 70, 53–59 (2017).
- X. Wendy Gu, J. R. Greer, Ultra-strong architected Cu meso-lattices. *Extrem. Mech. Lett.* 2, 7–14 (2015).

Acknowledgments: We thank J. K. Orbeck (Northwestern University) for providing editorial input. Funding: This material is based on work supported by the Air Force Office of Scientific Research award FA9550-22-1-0300 (crystal synthesis) and the Center for Bio-Inspired Energy Science, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences award DE-SC0000989 (SEM and TEM characterization). H.D.E. acknowledges the support of AFOSR award FA9550-20-1-0258 and ONR award N00014-22-1-2133. This work made use of the EPIC facility of Northwestern University's NUANCE Center, which has received support from the Soft and Hybrid Nanotechnology Experimental (SHyNE) Resource (NSF ECCS-2025633); the MRSEC program (NSF DMR-1720139) at the Materials Research Center; the International Institute for Nanotechnology (IIN); the Keck Foundation; and the State of Illinois, through the IIN. This research was supported in part through the computational resources and staff contributions provided for the Quest High Performance Computing Facility at Northwestern University, which is jointly supported by the Office of the Provost, the Office for Research, and Northwestern University Information Technology. Author contributions: Y.L., C.A.M., and H.D.E. conceived the idea. Y.L. designed and synthesized DNA and building blocks. Y.L. and W.Z. designed and synthesized the lattices. H.J. and Z.L. designed and performed the in situ mechanical experiments. Y.L. performed sample identification and SEM characterization and analysis before and after the in situ mechanical experiments. H.J. carried out the finite element analysis. H.J., H.D.E., and Y.L. analyzed the mechanics data. H.J., Y.L., H.D.E., and C.A.M. wrote the initial draft of the manuscript, H.J. and H.D.E. drafted the mechanics part. Z.W. and Y.L. did the TEM characterization. C.A.M. and H.D.E. supervised the project. All authors analyzed the data and contributed to the writing of the manuscript. Competing interests: The authors declare that they have no competing interests. Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials.

Submitted 17 July 2023 Accepted 30 August 2023 Published 29 September 2023 10.1126/sciadv.adj8103

ScienceAdvances

Ultrastrong colloidal crystal metamaterials engineered with DNA

Yuanwei Li, Hanxun Jin, Wenjie Zhou, Zhe Wang, Zhaowen Lin, Chad A. Mirkin, and Horacio D. Espinosa

Sci. Adv. 9 (39), eadj8103. DOI: 10.1126/sciadv.adj8103

View the article online https://www.science.org/doi/10.1126/sciadv.adj8103 Permissions https://www.science.org/help/reprints-and-permissions Downloaded from https://www.science.org at Northwestern University on October 01, 2023

Use of this article is subject to the Terms of service

Science Advances (ISSN 2375-2548) is published by the American Association for the Advancement of Science. 1200 New York Avenue NW, Washington, DC 20005. The title Science Advances is a registered trademark of AAAS.

Copyright © 2023 The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. No claim to original U.S. Government Works. Distributed under a Creative Commons Attribution NonCommercial License 4.0 (CC BY-NC).