- D. Hulin, A. Mourchid, R. Vanderhaghen, P. M. Fauchet, in Ultrafast Phenomena VII SE - 85, Springer Series in Chemical Physics. C. Harris, E. Ippen, G. Mourou, A. Zewail, Eds. (Springer, Berlin Heidelberg, 1990), vol. 53, pp. 282–284.
- K. Yabana, T. Sugiyama, Y. Shinohara, T. Otobe, G. F. Bertsch, Phys. Rev. B 85, 045134 (2012).
- 21. J. P. Perdew, A. Zunger, Phys. Rev. B 23, 5048-5079 (1981).
- R. Kienberger et al., Nature 427, 817–821 (2004).
 L. V. Keldysh, Sov. Phys. J. Exp. Theor. Phys. 20, 1307–1314
- L. V. Keldysh, Sov. Phys. J. Exp. Theor. Phys. 20, 1307 (1965).
- 24. D. Prendergast, G. Galli, Phys. Rev. Lett. 96, 215502 (2006).
- W. R. Thurber, R. L. Mattis, Y. M. Liu, J. J. Filliben, J. Electrochem. Soc. 127, 2291–2294 (1980).
- Soc. 127, 2291–2294 (1980).
 A. Srivastava, R. Srivastava, J. Wang, J. Kono, Phys. Rev. Lett. 93, 157401 (2004).
- 27. P. Radcliffe et al., New J. Phys. 14, 043008 (2012).
- 28. P. B. Allen, *Phys. Rev. Lett.* **59**, 1460–1463 (1987).

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NANOLITHOGRAPHY

Large-scale nanoshaping of ultrasmooth 3D crystalline metallic structures

Huang Gao,^{1,3*} Yaowu Hu,^{1,3*} Yi Xuan,^{2,3*} Ji Li,^{1,3} Yingling Yang,^{1,3} Ramses V. Martinez,^{4,5} Chunyu Li,^{3,6} Jian Luo,⁷ Minghao Qi,^{2,3} Gary J. Cheng^{1,3,8}†

We report a low-cost, high-throughput benchtop method that enables thin layers of metal to be shaped with nanoscale precision by generating ultrahigh-strain-rate deformations. Laser shock imprinting can create three-dimensional crystalline metallic structures as small as 10 nanometers with ultrasmooth surfaces at ambient conditions. This technique enables the successful fabrications of large-area, uniform nanopatterns with aspect ratios as high as 5 for plasmonic and sensing applications, as well as mechanically strengthened nanostructures and metal-graphene hybrid nanodevices.

anoscale metallic structures and their possible uses are under investigation in a variety of fields such as plasmonics (1), electronics (2), and biosciences (3). However, the largescale manufacture of such structures with high fidelity and quality [e.g., ultrasmooth surfaces, sharp corners, three-dimensional (3D) shapes, and high crystallinity] represents a substantial challenge. Although nanoimprint lithography is a useful method of fabricating nanometer-scale patterns on polymers (4, 5) and has been adapted to metallic glasses (6), direct nanoimprinting of crystalline metals is still generally infeasible because of the limitations on formability arising from (i) fluctuations of plasticity at the nanoscale caused by localized dislocation bursts (7, 8), (ii) size effects in plasticity (9, 10), and (iii) grain size effects, which generally limit the feature size to be larger than the grains (11, 12). These limitations can be circumvented by using nanocrystalline or amorphous metals (6), heating the sample close to melting temperature (13), or using a superhard mold (14). But these methods either place limits on the materials that can be used, or operate at high temperatures with serious drawbacks [e.g., the heating and solidification cycle in hot embossing (14) or melting (15) leads to high surface roughness, especially in sub-100-nm metallic structures]. Moreover, the low crystallinity in metallic glasses limits their functionality because of electric and magnetic losses (16). Similarly, fabrication of metal nanopatterns by direct nanoimprinting of nanoparticles (17) incurs size effects of the particles during their deposition into the nanomolds and is therefore not a good choice for ultrafine patterns. Currently, fabrication of metallic nanopatterns relies on timeconsuming, multistep approaches consisting of electron beam lithography (18, 19) or template stripping (20, 21). However, high resolution, high crystallinity, and low sidewall roughness cannot be achieved simultaneously, even with state-ofthe-art equipment.

Figure 1A summarizes the most common direct shaping processes, materials, ranges of their respective processing strain rates, and processing temperatures. A key barrier that impedes the fabrication of smooth ultrafine crystalline metallic 3D nanostructures is the high strain rate required to activate superplasticity in metals, due to the need of ultrafine grain/particle sizes to generate superplastic flows (22, 23). Unfortunately, the existing imprinting methods cannot provide sufficient high strain rates to generate 3D metallic crystalline nanostructures.

We demonstrate "laser shock imprinting" (LSI), a cost-effective direct nanoshaping method for high-throughput fabrication of smooth 3D crystalline nanostructures at ambient conditions. LSI uses a laser shock to compress metallic sheets into a silicon nanomold with a variety of shapes. We have used the nanomolds for over a hundred times with no damage or degradation in performance (fig. S1). This technique enables large-scale direct fabrication of smooth ultrafine metallic nanopatterns as small as 10 nm for mass production (fig. S2). LSI uses ultrahigh-strain rate deformation at room temperature to overcome the limitations in nanoscale formability of coarse-grained metals. Additionally, LSI can be applied to a broad range of metals, including metals as hard as Ti (fig. S3).

Figure 1B schematically illustrates the LSI process. We used a Nd:YAG laser pulse (0.3 to 1.4 GW/cm², wavelength 1064 nm, pulse duration ~5 ns) to irradiate an ablation coating layer (10 µm graphite) in direct contact with the sample. The sublimation of the ablation layer by the laser pulse generates a shock wave that, constrained by the confinement layer (glass or water), propagates through the metallic sheet and plastically deform it conformably on the underlying silicon mold with nanoscale resolution. According to Fabbro's model (24), the peak pressure of the shock wave generated by the laser pulse reaches 0.85 to 1.83 GPa, enabling the generation of strain rates on the order of 10^6 to 10^7 s⁻¹ during the laser shock, depending on the applied laser intensity and pulse duration.

We fabricated silicon nanomolds by e-beam lithography (EBL) and reactive ion etching (RIE) or wet etching. Atomic layer deposition (ALD) was used to deposit an ultrathin Al₂O₃ layer (5 to

¹School of Industrial Engineering, Purdue University, West Lafayette, IN 47907, USA ⁵School of Electrical and Computer Engineering, Purdue University, West Lafayette, IN 47907, USA ³Birck Nanotechnology Center, Purdue University, West Lafayette, IN 47907, USA ⁴Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA 02138, USA ⁵Madrid Institute for Advanced Studies, IMDEA Nanoscience, Ciudad Universitaria de Cantoblanco, 28049 Madrid, Spain. ⁶School of Materials Engineering, Purdue University, West Lafayette, IN 47907, USA. ⁷Department of NanoEngineering, University of California, San Diego, La Jolla, CA 92093, USA. ⁸School of Mechanical Engineering, Purdue University, West Lafayette, IN 47907, USA. *These authors contributed equally to this work. **†Corresponding** author. E-mail: gjcheng@purdue.edu

10 nm) to both increase the abrasive resistance of the nanomold and to help achieve the fabrication of sub-20-nm features in the Si wafers. We deposited an ultrathin layer (1 to 5 nm) of polyvinylpyrrolidone (PVP) or Au thin film (5 to 10 nm) on the surface of metal to act as a dry lubricant to reduce the friction during LSI processing and to improve the lateral resolution (fig. S4). Nonlubricant forming could also be used for ultrafine patterns (<30 nm) to ensure the precision.

Figure 2 shows several unique examples of metal nanostructures fabricated with LSI. Pyramidal nanostructures have been commonly used in surface-enhanced Raman scattering (SERS), due to the strong field enhancement achieved when surface plasmons propagating along nonadja-



Fig. 2. SEM images of several complex 3D nanostructures fabricated by LSI. (A) Ag nanopyramids.
(B) Ag fish-net (linewidth 30 nm, spacing 60 nm). (C) Nanobars with aspect ratio of ~3. (D) Array of nanogears imprinted on cold-rolled aluminum foil. (E) Array of triangular V-grooves (width 100 nm, depth 500 nm). (F) Array of nanotrenches (width 500 nm) in Ti thin film.

cent faces converge at the tip of the pyramid (21). Most of the pyramidal nanoarrays fabricated previously were not optimal in achieving a strong plasmonic enhancement, due to the large base size of the pyramids (5 to $20 \,\mu$ m), the amorphous structure of the plasmonic material, and the limited sharpness of the tip due to the metal deposition process. Figure 2A shows a large-area LSI of nanopyramids on the surface of a 2.5-µm-thick sheet of polycrystalline Ag (with micrometerscale grain size). The smooth surfaces and sharp tips of the pyramids indicate the outstanding formability induced by LSI. Pyramids with radius of curvature below 5 nm at their apex have been fabricated using a laser power of 1.4 GW/cm² (Fig. 2A, inset), and the possible mechanisms for forming such a sharp tip is discussed in supplementary materials. The sharpness of the nanotip greatly increases with the laser intensity (fig. S5).

The fabrication of nanoscale fishnet designs enabled the making of left-handed metamaterials with negative values of effective permittivity ϵ and permeability µ. Figure 2B shows a uniform fishnet structure (linewidth 30 nm, spacing 60 nm) fabricated on the surface of a polycrystalline Ag thin film by LSI. Currently, there is interest in the fabrication of hyperbolic metamaterials to realize useful functionalities in emerging metamaterials based on light (25). Unfortunately, the fabrication of many promising high-aspectratio periodic arrays of metallic nanostructures is difficult to achieve. LSI can fabricate smooth crystalline structures on Al thin foils with aspect ratios of ~3, as shown in Fig. 2C (width 220 nm, height 645 nm), using a laser intensity of 0.85 GW/cm². Higher aspect ratios could be achieved by increasing the laser intensity. Figure 2D shows an array of nanogears imprinted by LSI from a cold-rolled Al thin foil. The gear tooth sizes (length ~300 nm, height ~50 nm, width ~200 nm, radius at tooth bottom ~50 nm) are much smaller than the original grain sizes of the Al foil (~1.4 µm; see fig. S6A).

The triangular (V) groove-like nanostructures support the propagation of channel plasmon polaritons (26), which are attractive for applications in miniaturization of photonic circuits (27). Most V-grooves are fabricated by FIB, which is a very slow and low-volume prototyping process. With LSI and a suitable Si mold, we achieved a large-area array of nanoscale V-grooves with aspect ratios of 1:5 (width 100 nm, height 500 nm, V-angle 14°) and sharp side walls in Ag (Fig. 2E), with laser intensity of 0.334 GW/cm².

LSI is also a suitable technique to pattern hard metals, such as Ti with a melting temperature of 1668°C and a Vicker's hardness 5 times that of aluminum. The ultrasmooth nanostructures fabricated on the surface of a 2.5-µm-thick layer of Ti (Fig. 2F and fig. S3) demonstrate its good formability using LSI. We recognize that LSI, at its present level of development, still has some limitations, including the relatively high fabrication cost of the nanomolds (which, however, can be reused for hundreds of imprintings). It is also a challenge to transfer the imprinted metal nanostructures onto another substrate. LSI, however, is versatile and scalable and, with an appropriate choice of materials for the nanomolds and selection of laser shock conditions, could enable high-throughput fabrication of sub-10-nm 3D nanostructures.

Morphological fluctuations during microscale deformation at low strain rates can result from the generation of localized dislocation avalanches (9, 10). Our results, however, show that LSI, at high strain rates, enables the direct imprinting over large areas of uniform and smooth arrays of complex nanofeatures on the surface of crystalline metals. LSI overcomes both the limit of nanoscale formability of metallic materials and the size effect at the nanoscale.

To understand the underlying mechanisms of LSI, we investigated the microstructure of Al nanobars imprinted with LSI by combining highresolution transmission electron microscopy (HRTEM) with molecular dynamics (MD) and finite element method (FEM) simulations. The methods and results are documented in supplementary materials, which are briefly summarized in Fig. 3 and the following text. The as-received Al sample has only one large grain through film thickness (fig. S6). After LSI, significant reductions in and nonuniform distribution of grain sizes can be observed. HRTEM images (Fig. 3B and fig. S6B) show that relatively large grains are present within and around the nanobars, while small grains with sizes of tens of nanometers are present in between the nanobars. The corresponding inverse fast Fourier transform (IFFT) images (Fig. 3C) reveal a low dislocation density inside the patterned nanostructures, while higher dislocation densities are found near the corners of the nanostructures. From MD simulation, strains around the edges and corners of the nanomold are much higher than at areas inside the nanomold (Fig. 3A). The relative low dislocation density within the patterned nanostructures can be explained from the nanoscale geometrical confinement effect on the propagation of dislocation (10) and, possibly, by a low-temperature dynamic recrystallization, which is often found at high strain rate deformation (28) and supported by our MD simulation (Fig. 3A) in that the strain field inside the nanomold is much lower than that outside of the nanomold. A local temperature rise inside the nanomolds, which is supported from FEM simulation (fig. S7), also facilitates dynamic recrystallization. In LSI, the nanosized grains formed at the initial stage of deformation are the keys to the nanoscale formability. This can be explained by the coalescence of dislocations and their reorganization into grain boundaries to reduce grain sizes during the imprinting process; subsequently, grain boundaries act as dislocation sources and sinks, which leads to the ultrasmooth nanoshaping. Grain boundary disordering, as indicated by MD simulation (fig. S9), can also serve as an effective sink to adsorb dislocations. This interaction between dislocations and grain boundaries hinders dislocation avalanches and strain burst, promoting a uniform deformation and maintaining smooth surfaces. Additionally, the large surface area of the nanopatterned structures can further absorb the dislocations during the LSI process. This hypothesized mechanism is consistent with our MD simulation (figs. S8 to S11) and a prior study (9) which suggested that grain boundaries hinder avalanche propagation and that the size of strain bursts is reduced when the grain size decreases.

Shown in Fig. 3, D and E, are the different microstructures of Al and Ag nanopyramids fabricated using the same Si nanomold (base width 800 nm) and laser intensity (0.87 GW/cm²). For Al, a relative high stacking fault energy facilitates the cross-slip of partial dislocations, and the recrystallization temperature is low (175°C). As a result, Al nanopyramids are largely converted into single grains and low-angle grain boundaries are dominant in the microstructure (Fig. 3D). On

the other hand, face-centered cubic (fcc) metals with low stacking fault energies that result in large separations between the partial dislocations such as Au and Ag, are difficult to have cross-slip and prone to work hardening. The dislocation density in these materials is increased by the successive generation of dislocations. Additionally, the high recrystallization temperature (970°C for Ag) impedes the efficient reorganization and annihilation of the dislocations. Figure 3E shows the microstructure of the Ag nanopyramids, in which low-angle grain boundaries and nanotwinning (with 60° misorientation) are dominant.

LSI not only improves the formability of materials but also the hardness of the fabricated nanostructures. Figure S12 shows the typical loading and unloading curves of as-received Al



Fig. 3. Results of MD simulation and TEM characterization of imprinted specimens. (**A**) MD simulation results showing the strain distribution during LSI of a single crystal of AI (thickness 8 nm) to a nanomold (width and depth, 16.44 nm). (**B**) Cross-sectional STEM images of an AI thin film after LSI. Dark-field STEM image at high magnification showing the grain structure between the nanobars. HRTEM image of a large-angle grain boundary in the nanobar, showing the lattice structure of the crystals within and around the nanobars. (**C**) The corresponding IFFT image of the area within and around the nanobars. (**D** and **E**) TEM and grain boundary misorientation distribution of (D) an AI nanopyramid and (E) an Ag nanopyramid.

foil and the LSI processed Al foil during a nanoindentation cycle. The hardness of as-received samples is ~0.37 GPa, whereas the hardness at the nanobars fabricated by LSI is ~0.64 GPa. The improved strength of the nanostructures fabricated by LSI correlates with grain/subgrain refinement (fig. S13) and the number of residual dislocation structures (fig. S14).

Metamaterial perfect absorbers (MPAs) have attracted great attention for potential applications in emitter, sensing, detection, and wireless communication (29). Although MPAs operating at microwave and terahertz frequencies with micrometer structures could be easily achieved, fabricating nanometer features for visible and ultraviolet regions remains a challenge because of limited nanofabrication methods. Periodic aluminum nanotrenches with 10-, 20-, and 30-nm gaps were fabricated using the LSI method in a fast and inexpensive way via a single laser shot (laser intensity of 0.61 GW/cm²) on a silicon nano-

mold (Fig. 4, B to D). We used atomic force microscopy (AFM) to confirm the ultrasmooth topography of the Al nanotrenches (fig. S2) and finite-difference time domain (FDTD) simulations to calculate the dependence of the absorbance over the gap width (Fig. 4E). The results revealed that the Al nanotrenches with 30-nm gaps have near-perfect absorption at $\lambda = 436$ nm (fig. S15 and fig. S16, A and B), thereby demonstrating MPA with a visible band. The surface-enhanced Raman scattering (SERS) of the Al nanotrenches fabricated by LSI depends on the matching of the incident and exciting radiation with plasmons on the substrate, which is controlled by the geometry of the fabricated structures. Figure 4F shows the application of Al nanopatterns fabricated by LSI as SERS substrate for graphene with an enhancement up to three orders of magnitude for the G and 2D peaks of graphene.

As a high-strain rate, cold-forming process, LSI is also suitable for the fabrication of hybrid

nanostructures. Figure 4G illustrates the formation of graphene-metal hybrid nanostructures by direct imprinting a single layer of graphene grown on Cu foil and forming a graphene nanogap. Figure 4H shows the SEM image after deformation of graphene-Cu thin film into nanogaps by LSI with corresponding AFM image. The local field is probed using a near-field scanning optical microscope (NSOM) (Fig. 4I). As shown in the NSOM image, a high-intensity region has been detected at the center of the nanogap with laser excitation wavelength 633 nm. Because of the resolution limit of the NSOM tip, the two hot spots located at the structural corners are merged during the experiment, resulting in a single high-intensity slit. Graphene can be strained without breaking under certain conditions. The strainability of graphene by deforming to 3D nanoscale surface has been studied (30). Figure 4J shows the Raman spectrum of the graphene-Cu thin film after LSI under several laser conditions. When the laser



Fig. 4. Various ultrasmooth metallic and metal-graphene nanostructures made by LSI with enhanced electromagnetic and optical properties. (A) Schematic picture of transferring graphene on nanoshaped meal structures for SERS measurements. (**B** to **D**) SEM images of periodic aluminum trenches (10, 20, and 30 nm) after LSI, and an AFM image showing the ultrasmooth topography of the Al trench. (**E**) Absorption at $\lambda = 630$ nm of the Al nanotrenches fabricated by LSI vs. the gap width of the nanopatterns. (**F**) SERS measurement of nanopatterned Al with various gap width. (**G**) Illustration of the formation of graphene-Cu hybrid nanogaps, and transferring of

graphene to Au nanopyramid arrays. (**H**) SEM and AFM image of a graphene-Cu nanogap after LSI (0.6 GW/cm²). (**I**) Results on local field enhancement of the graphene-Cu nanogap by FDTD simulation and NSOM measurement. (**J**) Raman spectrum of graphene on SiO₂, graphene on Cu and nanopatterned graphene-Cu structures by LSI (0.5 GW/cm², 0.6 GW/cm²). (**K**) Illustration of transferring graphene to Au nanopyramid arrays. (**L**) FDTD simulations results showing the field enhancement around the tip at the resonant frequency. (**M**) Raman spectra showing enhancement of Raman signatures of graphene on nanopyramid compared with that on flat surfaces. intensity is larger than 0.6 GW/cm², graphene will be cut into nanogaps (Fig. 4H). The Raman spectrum shows that D peak (related to defect level) is high, while G peak is not shifted relative to that in the unstrained graphene, since strain is released after cut. When the laser intensity is less than 0.5 GW/cm², the graphene is continuous and conformal on nanoshaped Cu. This is indicated in the Raman spectrum (Fig. 4J) where the D peak is low and the G peak is shifted to the left because of straining.

In order to study the SERS of nanopyramids, graphene is transferred onto the Au nanopyramids array (Fig. 4K) to measure the localized plasmonenhanced Raman spectra and verify the enhancement of the Raman signatures of graphene. As shown in Fig. 4M, the Raman signature of a monolayer of graphene (both G and 2D peak) is highly increased when it is placed on top of the nanopyramids, demonstrating the capability of local field enhancement of these structures. The ratio of 2D/G intensities has decreased from around 3 to 1, which could be a result from charge doping of graphene from the imprinted plasmonic nanostructures under laser excitation. FDTD simulations confirmed the field enhancement around the tip at the resonant frequency (Fig. 4L and fig. S16, C and D).

LSI is a high-throughput 3D nanoimprinting technique capable of producing nanoscale crystalline metallic nanostructures over a 6-inch wafer within 30 s, using laser pulses (pulse energies of 150 to 250 mJ, a beam size of 3 mm, and pulse frequency of 10 Hz). The crystalline nanostructures fabricated by LSI have several characteristics that make them especially suited for electronic, plasmonic, or sensing applications: (i) precise and ultrasmooth nanoshaping due to better formability and low-temperature processing; (ii) complex 3D nanoshaping, sub-20-nm lateral sizes, and aspect ratios up to 5 when fabricated using silicon nanomolds; (iii) beneficial crystalline metallic nanostructure for device performance, because it has the potential to improve electronic stability and to reduce optical loses, noise, and energy consumption. Our results show that LSI has the potential to provide new insights into the role of crystallinity in the electronic, optical, and mechanical behavior of metallic nanostructures. Further, LSI is an attractive fabrication method for the development of future electronics, optics, and sensing devices.

REFERENCES AND NOTES

- 1. L. Yin et al., Nano Lett. 5, 1399-1402 (2005).
- 2. E. Ozbay, Science 311, 189–193 (2006).
- 3. J. R. Lakowicz, *Plasmonics* **1**, 5–33 (2006).
- S. Y. Chou, P. R. Krauss, P. J. Renstrom, Science 272, 85–87 (1996).
- 5. L. J. Guo, Adv. Mater. 19, 495–513 (2007).
- G. Kumar, H. X. Tang, J. Schroers, *Nature* **457**, 868–872 (2009).
 M. D. Uchic, P. A. Shade, D. M. Dimiduk, *Annu. Rev. Mater. Res.* **39**, 361–386 (2009).
- 8. J. R. Greer, J. T. M. De Hosson, Prog. Mater. Sci. 56, 654–724 (2011).
- F. F. Csikor, C. Motz, D. Weygand, M. Zaiser, S. Zapperi, Science 318, 251–254 (2007).
- M. D. Uchic, D. M. Dimiduk, J. N. Florando, W. D. Nix, *Science* 305, 986–989 (2004).
- F. Vollertsen, H. Schulze Niehoff, Z. Hu, Int. J. Mach. Tools Manuf. 46, 1172–1179 (2006).

- 12. W. Kurnia, M. Yoshino, J. Micromech. Microeng. 19, 125028 (2009).
- 13. S. Y. Chou, C. Keimel, J. Gu, Nature 417, 835-837 (2002).
- 14. K. A. Lister et al., J. Vac. Sci. Technol. B 22, 3257-3259 (2004).
- 15. B. Cui, C. Keimel, S. Y. Chou, Nanotechnology 21, 045303 (2010).
- 16. R. F. Oulton, Nat. Photonics 6, 219-221 (2012).
 - 17. C. C. Liang et al., Opt. Express 19, 4768-4776 (2011).
 - 18. N. Yu et al., Science 334, 333–337 (2011).
 - 19. J. Lin et al., Science 340, 331-334 (2013).
 - 20. W. Zhou, T. W. Odom, Nat. Nanotechnol. 6, 423-427 (2011).
 - 21. P. Nagpal, N. C. Lindquist, S. H. Oh, D. J. Norris, Science 325,
 - 594–597 (2009). 22. R. S. Mishra, T. R. Bieler, A. K. Mukherjee, *Acta Metall. Mater.* 43. 877–891 (1995).
 - T. G. Nieh, J. Wadsworth, T. Imai, Scr. Metall. 26, 703–708 (1992).
 - R. Fabbro, J. Fournier, P. Ballard, D. Devaux, J. Virmont, J. Appl. Phys. 68, 775–784 (1990).
 - A. Poddubny, I. Iorsh, P. Belov, Y. Kivshar, *Nat. Photonics* 7, 948–957 (2013).
 - S. I. Bozhevolnyi, V. S. Volkov, E. Devaux, T. W. Ebbesen, *Phys. Rev. Lett.* **95**, 046802 (2005).
 - D. K. Gramotnev, S. I. Bozhevolnyi, Nat. Photonics 4, 83–91 (2010).
 - Q. Li, Y. Xu, Z. Lai, L. Shen, Y. Bai, J. Mater. Sci. Technol. 15, 435 (1999).

- C. M. Watts, X. Liu, W. J. Padilla, Adv. Mater. 24, OP98–OP120 (2012).
- J. Li, T. F. Chung, Y. P. Chen, G. J. Cheng, *Nano Lett.* 12, 4577–4583 (2012).

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SUPPLEMENTARY MATERIALS

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MEMBRANES

Metal-organic framework nanosheets as building blocks for molecular sieving membranes

Yuan Peng,^{1,2} Yanshuo Li,^{1*} Yujie Ban,^{1,2} Hua Jin,^{1,2} Wenmei Jiao,^{1,2} Xinlei Liu,¹ Weishen Yang^{1*}

Layered metal-organic frameworks would be a diverse source of crystalline sheets with nanometer thickness for molecular sieving if they could be exfoliated, but there is a challenge in retaining the morphological and structural integrity. We report the preparation of 1-nanometer-thick sheets with large lateral area and high crystallinity from layered MOFs. They are used as building blocks for ultrathin molecular sieve membranes, which achieve hydrogen gas (H₂) permeance of up to several thousand gas permeation units (GPUs) with H₂/CO₂ selectivity greater than 200. We found an unusual proportional relationship between H₂ permeance and H₂ selectivity for the membranes, and achieved a simultaneous increase in both permeance and selectivity by suppressing lamellar stacking of the nanosheets.

as separation with membranes is an energyefficient and environmentally friendly alternative to cryogenic and adsorptive or absorptive gas separation processes. Polymer membranes are subject to a trade-off between productivity (permeability) and efficiency (selectivity), known as Robeson's upper bound (*I*, *2*). Membranes based on molecular sieve materials are expected to overcome this limitation by relying on their ability to distinguish molecules based on size and shape (*3–8*). Molecular sieve nanosheets (MSNs) with large lateral area and small thickness are the most appropriate building

yangws@dicp.ac.cn (W.Y.)

blocks for ultrathin, and thus ultrapermeable, molecular sieve membranes (9). The permeance of such membranes is measured in gas permeation units (1 GPU = 10^{-6} cm³ cm⁻² s⁻¹ cmHg⁻¹ at STP). Tsapatsis et al. demonstrated the fabrication of molecular sieve membranes based on exfoliated zeolite nanosheets with thickness at the unit cell level (~3 nm) (10), whereas the types of zeolites that can be easily exfoliated are rather limited (11). Recently, graphene oxide (GO) nanosheets with selective defects were used to produce ultrathin membranes with thickness of as low as 1.8 nm (12). However, the measured H_2 permeance of these extremely thin GO membranes, ~300 GPUs, was still at the same level as conventional microporous membranes (13). This can be attributed to the low density of selective defects and their random distribution in the GO nanosheets.

¹State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China. ²University of Chinese Academy of Sciences, Beijing 100049, China. ***Corresponding author. E-mail: leeys@dicp.ac.cn (Y.L.);**





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