Toward digitally controlled catalyst architectures: Hierarchical nanoporous gold via 3D printing

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Monolithic nanoporous metals, derived from dealloying, have a unique bicontinuous solid/void structure that provides both large surface area and high electrical conductivity, making them ideal candidates for various energy applications. However, many of these applications would greatly benefit from the integration of an engineered hierarchical macroporous network structure that increases and directs mass transport. We report on 3D (three-dimensional)—printed hierarchical nanoporous gold (3DP-hnp-Au) with engineered nonrandom macroarchitectures by combining 3D printing and dealloying. The material exhibits three distinct structural length scales ranging from the digitally controlled macroporous network structure (10 to 1000 μm) to the nanoscale pore/ligament morphology (30 to 500 nm) controlled by dealloying. Supercapacitance, pressure drop, and catalysis measurements reveal that the 3D hierarchical nature of our printed nanoporous metals markedly improves mass transport and reaction rates for both liquids and gases. Our approach can be applied to a variety of alloy systems and has the potential to revolutionize the design of (electro-)chemical plants by changing the scaling relations between volume and catalyst surface area.

INTRODUCTION

Monolithic nanoporous metals, often created by a combination of alloying and dealloying steps, are composed of a tortuous, bicontinuous network of nanoscale pores and metallic ligaments. These unique structural characteristics make monolithic nanoporous metals ideal candidates for a broad array of applications that require fast simultaneous mass, thermal, and electron transport (1). In dealloying, the nanoporous metal’s bicontinuous structure is produced by selective removal of the less noble constituent of a multicomponent (most commonly binary) alloy under corrosive conditions (2). For example, nanoporous gold (np-Au) can be formed by selective dissolution of silver (Ag) from Ag-Au alloys, often using nitric acid as the corrosive etching agent. The nanoporous metal morphology (and feature size) can be tuned with material and process parameters (for example, initial alloy composition, selection of specific corrosion chemistry and corrosive chemical agents, choice of electrolyte, applied electric potential, and dealloying time), where production of nanoporous metals with unimodal pore and ligament size distributions is most widespread (3). Nanoporous metals are valued for their physical, structural, mechanical, thermal, and functional properties including open-cell porosity (typically ~70% by volume), large surface area–to–volume ratios, mechanical resilience, and high thermal and electrical conductivities (4). However, bulk nanoporous metals are also known to suffer from transport limitations, where diffusion-based mass transport through the tortuous nanoporous network is sluggish, limiting the accessible surface area and ultimately diminishing the benefits of using bulk nanoporous metals for (electro-)catalysis (5, 6), sensors (7), actuators (8), electrochemical energy systems (9), and chemical separations and chromatography (10). Compared to their nonhierarchical counterparts, nanoporous metals with structural hierarchies—those found in nature such as in lungs and vasculature—can overcome these limitations by incorporating macroporous transportation “highways” that span many length scales, thus ensuring that the surface area is large yet remains accessible. Realization of rapid, directional transport requires the development of new fabrication techniques that generate engineered, anisotropic macropore architectures.

Previous studies have attempted to fabricate isotropic hierarchically structured bulk nanoporous metals (2, 11–13). For example, strategies have been developed to generate np-Au with bimodal pore size distributions by multiple annealing and (re-)dealloying steps with sequential Ag removal (2, 11, 12). Hierarchical np-Au has been obtained by coating sacrificial polymer templates with Ag-Au alloy films followed by removal of polymer and Ag (13). Yet, these fabrication approaches suffer from limited material flexibility and, more importantly, fail to produce deterministic, ordered, and anisotropic hierarchical structures needed to tailor mechanical behavior and direct transport for emerging applications such as three-dimensional (3D) chemical reactors, advanced catalytic systems, flow batteries, and flow-through electrodes. Now, we demonstrate architected nanoporous metals with control over multiple scales of structure, achieved by combining “bottom-up” alloying and dealloying processing routes with “top-down” 3D printing methods.

Recently, 3D printing and additive manufacturing methods have been used to fabricate complex, multiscale architectures that break traditional scaling laws and lead to previously unobtainable combinations of structural, mechanical, chemical, thermal, and functional properties (14–17). Here, we report 3D printing of Au and Ag “inks” with a room temperature, extrusion-based 3D printing technique, known as direct ink writing (DIW), which, when combined with alloying and dealloying processes, creates hierarchical nanoporous metal architectures composed of np-Au. Our 3D-printed hierarchical nanoporous gold (3DP-hnp-Au) structures markedly increase electric field–driven ion transport (up to 10 times) and pressure-driven mass transport (up to 105 times). Our printing process uses a three-axis positioning system to print 3D architectures by extruding a continuous filament through a microscale nozzle and building up structures in...
a layer-by-layer fashion \(^{(18)}\). While ceramic \(^{(19)}\), metallic \(^{(20)}\), polymeric \(^{(21)}\), and other carbon-based inks \(^{(22, 23)}\) have been developed for printing a broad array of functional devices \(^{(24)}\), composite inks that allow controlled integration of nanopores by dealloying to yield hierarchical nanoporous metals have not been demonstrated.

**RESULTS**

3DP-hnp-Au samples were prepared with a series of printing, annealing, and dealloying steps (Fig. 1). First, we created a viscous, paste-like ink composed of a mixture of Ag and Au microparticles with an overall atomic ratio of Ag/Au = 70:30. This alloy composition was selected because it results in mechanically robust np-Au structures after dealloying \(^{(25)}\). The ink lowers its viscosity in the presence of shear flows, enabling printing at moderate pressures, and undergoes rapid modulus recovery upon exiting the nozzle to achieve the requisite shape retention for successful 3D printing (fig. S1) \(^{(26)}\). To create 3D architectures, we loaded the ink into a syringe barrel, removed any trapped gas from the ink mixture, affixed a micro-

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**Fig. 1.** 3DP-hnp-Au exhibits control over structure that spans over seven orders of magnitude in length scales, from centimeters to nanometers. (A to C) Schematic illustrations of (A) 3D printing inks composed of mixtures of Au and Ag microparticles, polymer binder, and solvent (binder and solvent are represented as a green color). (B) The annealing step alloys the Au and Ag phases and removes the polymer binder to yield microscale porosity. (C) The dealloying step selectively removes the Ag phase, yielding the nanoscale porosity. Optical images of the 1-mm scale for multilayer woodpile-like architectures for printing (D), annealing and alloying (E), and dealloying steps (F). Scanning electron microscopy (SEM) images are shown depicting the structural evolution after the printing, annealing (and alloying), and dealloying steps for the 100-μm scale (G to I), 10-μm scale (J to L), 1-μm scale (M to O), and 100-nm scale (P to R). (S and T) Coarsening of the nanostructure after reannealing. Scale bars, 1 mm (D to F), 100 μm (G to I), 10 μm (J to L), 1 μm (M to O and S), and 100 nm (P to R and T).

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The as-printed, green-body parts consisted of discrete Au and Ag particles bound by polymer. To form homogeneous Ag-Au alloys, the printed structures undergo heat treatment at 850°C for 12 hours in air (Fig. 1B). The diffusion length, \(L\), was estimated using Fick’s law, \(L = (2D\cdot t)^{1/2}\), where \(D\) is the diffusion coefficient and \(t\) is the diffusion time. Here, \(D\) is defined as \(D_0\exp(-E_a/RT)\), where \(D_0\) is the temperature-independent diffusion coefficient (cm\(^2\)/s), \(E_a\) is the activation energy for diffusion (cal/mol), \(R\) is the gas constant [J/(mol·K)], and \(T\) is the absolute temperature (K). Using reported values \(^{(27)}\) for \(D_0\) and \(E_a\) (\(D_0 = 0.23\) cm\(^2\)/s and \(E_a = 43.54\) cal/mol for diffusion of Ag in Au and \(D_0 = 0.35\) cm\(^2\)/s and \(E_a = 46.67\) cal/mol for diffusion of Au in Ag, respectively), the diffusion length for Ag in Au and Au in Ag at 850°C for 12 hours is calculated to be 80 and 57 μm, respectively. This is well above the Au and Ag particle size of 10 to 20 μm, thus producing a homogeneous alloy. In addition, thermal decomposition of the polymeric binder creates microscale porosity within the printed features. In the last step, nanoscale porosity is introduced by
Our 3DP-hnp-Au has a hierarchical structure that spans over seven orders of magnitude in length scales—from centimeters to nanometers. The longest length scale (that is, the macroscale) is directly controlled by the 3D printing process and is thus the most deterministic in its structure and direction. The printing process defines the sample shape and creates the macroscale architecture, which is composed of filaments with feature sizes that are typically on the order of 100 μm with center-to-center spacing between filaments (for example, the macropores) that can span from 10 μm to over 1 mm in distance (Fig. 1, D to F). The next level of structure consists of microscale pores (~1 to 10 μm) created by solvent evaporation and degradation of the polymer binder (Fig. 1, J to L). The particles are alloyed upon annealing (Fig. 1, M and N), and the dealloying step (Fig. 1O) creates nanoscale porosity with ligaments and pores sizes on the order of ~10 to 100 nm (Fig. 1, P to R). Adding a second annealing step after dealloying coarsens the nanoscale structure, enlarging it from the nanoscale to the microscale (Fig. 1, S and T) (28, 29).

We note that the woodpile-like, as-printed structures have ~150-μm filament diameters with ~300-μm center-to-center spacing between filaments. The as-printed structures are tan-colored (Fig. 1D). They turn to a white silvery color upon alloying (Fig. 1E) and convert to a dark golden color upon dealloying (Fig. 1F). These color changes are caused by both compositional and structural changes that occur during the postprinting processing steps. Heat treatment leads to a small amount of volumetric shrinkage (~10%), while negligible shrinkage is observed after dealloying. The as-printed structures are composed of densely packed mixtures of Au and Ag microparticles with small pores (Fig. 1, G and J). Upon annealing, large faceted grains form because of Au and Ag particle fusing and coarsening, leading to Ag-Au alloy formation (Fig. 1, H, K, N, and Q). The microscale total porosity and pore size are adjusted by tuning the total solvent and polymer binder content. Dealloying forms 3DP-hnp-Au with ligament and pore feature sizes of ~40 nm (Fig. 1, O and R). The cross-sectional view of a fractured filament confirms the uniformity of the nanoporous structure throughout the dealloyed filaments (Fig. 2). Energy-dispersive x-ray spectroscopy (EDS) analysis of 3DP-hnp-Au reveals ~2 atomic % (at %) of residual Ag that is similar to the residual Ag content of bulk np-Au obtained through free corrosion (30). Figure 1 (S and T) shows that the nanoscale feature size increases from ~40 to 500 nm by reannealing at 500°C for 1 hour. This second annealing step only affects the nanoscale structure because the temperature is not high enough or the time is long enough to significantly coarsen the longer length scale structure formed during the initial 850°C annealing step applied for alloy formation. The ligament size distributions of np-Au and 3DP-hnp-Au before and after annealing are 50 ± 11 nm, 40 ± 7 nm, and 552 ± 114 nm, respectively (fig. S2).

The 3D printing process used for this work enables deterministic patterning of the overall sample shape and microscale architecture (Fig. 3). A test pattern consisting of parallel lines with systematically changing center-to-center filament spacing was used to determine the resolution limit of the Ag-Au composite ink. For a 200-μm-diameter feature size, a filament spacing as short as ~50 μm was achieved (Fig. 3A). The minimum possible printed feature size depends on the ink particle size and rheology. Replacing microscale particles used in this study with nanoparticles should enable patterning of finer features. We also demonstrated printing multilayer structures, including spiral, honeycomb, hollow pillar array, and square and radial lattice structures (Fig. 3, B to F). Figure 3 (B to D) consists of 2D extruded structures where the upper layers are fully supported by the underlayers, whereas the square and radial lattice structures in Fig. 3 (E and F) have features that must span gaps in the underlying layers. The relative density of the periodic 3DP-hnp-Au structures can be tuned over a wide range by changing the filament diameter and spacing.

The multiscale hierarchical structure of 3DP-hnp-Au improves the electrokinetic flow through electrolyte-filled pores, as demonstrated by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) (Fig. 4). The electrochemically accessible surface areas of both np-Au and 3DP-hnp-Au were determined using the Au oxide stripping technique. The technique assumes that, after performing a positive sweep, the Au surface is covered with a monolayer of oxygen, which is then reduced during the negative scan (Fig. 4A). Both materials have very similar gravimetric surface areas, 5 m²/g for np-Au versus 4.7 m²/g for 3DP-hnp-Au. The measured surface areas of np-Au are consistent with previously reported values (2, 31), and their similarity is a result of their comparable nanoscale ligament size, which, for both np-Au and 3DP-hnp-Au, is about 40 nm in diameter. EIS, collected at open-circuit potential in 0.5 M H₂SO₄ solution, was performed to assess ion transport limitations by measuring the frequency response of the capacitance and thus the electrokinetic flow induced by small perturbations of the electric field. Nyquist plots reveal that both np-Au and 3DP-hnp-Au exhibit a pure capacitive response (fig. S3). The capacitance-frequency plots show the expected decrease in capacitance with increasing frequency (Fig. 4B). At low frequencies, both materials exhibit similar capacitance values consistent with their comparable specific surface areas. However, the frequency where the capacitance decreases to 50% of its low frequency (10⁻² Hz) threshold value is about 10 times higher for the 3DP-hnp-Au sample. The improved rate performance of the 3DP-hnp-Au sample directly reflects the faster electrokinetic flow.

Fig. 2. Fracture surfaces show that the structure is uniform throughout the dealloyed filaments. (A) SEM image showing fracture surface of a dealloyed filament. The large grains and faceted surfaces were formed during annealing. (B) Higher-resolution SEM image of the fracture surface and (C) highest-resolution SEM image of the fracture surface showing that nanoscale ligament and pore morphology extend throughout the volume of the printed filaments. Scale bars, 10 μm (A), 1 μm (B), and 100 nm (C).
through the electrolyte-filled pores. The macroscopic charging kinetics were evaluated by performing potential jump experiments in the double-layer region, where only nonfaradic processes occur. First, the sample was held for 60 s at an initial potential $E_i = 0$ V (versus Ag/AgCl) until the surface was fully charged, followed by a potential jump to 0.6 V (versus Ag/AgCl) while monitoring the transient current response (Fig. 4C). The charging kinetics were evaluated by comparing the time ($t_{1/2}$) at which the current decayed to its half-maximum value. $3DP$-hnp-Au ($t_{1/2} = 0.38$ s) charges about two times faster than np-Au ($t_{1/2} = 0.67$ s), thus confirming the improved mass transport properties of $3DP$-hnp-Au observed in the EIS experiments.

The multiscale hierarchical structure of $3DP$-hnp-Au also enhances pressure gradient–driven mass transport compared to its np-Au counterpart (Fig. 5). The transport properties for liquids were assessed in a custom flow-through cell setup by measuring the pressure drop across np-Au and $3DP$-hnp-Au membranes as a function of flow speed (Fig. 5A). Pressure drop calculations were performed on the basis of a fiber bed model for np-Au and a square tube model for $3DP$-hnp-Au and compared against pressure drop measurements for both materials (Fig. 5B). The np-Au pressure drop exceeded the upper limit of the pressure sensor (103.4 kPa) for all tested flow speeds. Calculations predict a pressure drop of more than $10^5$ kPa across the nonhierarchical np-Au membrane. By comparison, $3DP$-hnp-Au exhibits a pressure drop of less than 6.8 kPa for all tested flow speeds. The overall pressure drop in a single channel of the square lattice of $3DP$-hnp-Au is expected to originate from both viscous effects associated with tube flow and the smaller diameter.
outlet at the tube end, which originates from a partial sidewall collapse during the printing process (Fig. 1D). To determine which effect dominates, we first performed laminar pressure drop calculations, which resulted in an order-of-magnitude lower pressure drop than the experimental observation. In addition, pressure drop experiments show nonlinear scaling behavior, which further rules out viscous effects. The experimentally observed nonlinear pressure drop and flow rate dependence, as confirmed by computational fluid dynamics simulations and approximated by Bernoulli’s equation (that is, eq. S4), all suggest that the pressure drop is dominated by the smaller diameter outlet at the tube exit. Calculation results agree with the experimental data (Fig. 5B and figs. S4 and S5).

Nanoporous Au-derived catalysts have shown excellent long-term stability. Compared to their supported Au nanoparticle–based counterparts, they seem to be less prone to deactivation due to Ostwald ripening and particle migration/coalescence that together rapidly decrease reaction rates (30, 32). On the other hand, bulk np-Au catalysts are plagued by mass transport limitations. Now, hierarchical np-Au catalysts, especially those derived from combining emerging 3D printing and design optimization methods, promise to overcome these transport limitations. To demonstrate the benefits of introducing a hierarchical 3D structure on catalysis, we compared reactions of np-Au and 3DP-hnp-Au in a flow-through cell setup (Fig. 5C) and examined the selective partial oxidation of alcohols (Fig. 5D) (5, 9, 33). These catalyst materials presented comparable selectivity (70 to 90%) of methyl formate formation from methanol, which confirms that np-Au and 3DP-hnp-Au have similar surface chemistries. However, differences emerge when comparing the reaction rate per catalyst mass, with the 3DP-hnp-Au catalyst outperforming np-Au by two times for this metric (Fig. 5D). This result points to a more efficient use of the available material (and catalytic sites) in 3DP-hnp-Au and is a direct manifestation of improved transport characteristics. Previous work on nonhierarchical catalyst membranes revealed that most catalytic reactions occur near the gas flow–facing side of the catalyst membrane if chemical reactions are fast compared to mass transport within the porous catalyst membrane (34). The higher reaction rate per catalyst mass of the 3DP-hnp-Au catalyst membrane thus reveals that a larger fraction of the internal catalyst surface contributes to the observed reactivity. The experiment also proves that the combined action of annealing and subsequent ozone treatment effectively removes all carbon residues from the organic binder of the Ag-Au DIW ink. Improving the resolution and feature size of our 3D printing process by using Ag-Au nanoparticle–based inks is expected to further improve the efficiency of 3DP-hnp-Au catalyst architectures.

The mechanical properties of our 3DP-hnp-Au samples are important for many potential applications, especially if they involve pressure gradients across the material. As a preliminary test of the mechanical properties of the 3DP-hnp-Au materials described in this paper, we performed a macroscopic uniaxial compression test with a 4% relative density sample (that is, relative to bulk gold density, so the porosity is 96%). The corresponding stress-strain curve is shown in fig. S7. The tested sample remained monolithic throughout the compression test, revealing its high ductility. The compressive strength (taken to be the intersection between the initial loading region and the following stress plateau) of the 4% relative density 3DP-hnp-Au sample is about 1 MPa, which is ~10 to 15 times lower than the value reported for nonhierarchical np-Au with a ~7 times higher density (~0.3) and similar ligament diameters (30 to 40 nm) (35). The observed decrease in compressive strength with relative density is consistent with the Gibson and Ashby foam plasticity model, which predicts that the strength scales with the relative density to the power of 3/2 (36). Therefore, our 3D printing approach enables the density of np-Au

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**Fig. 5. Transport and catalytic reactions in np-Au and 3DP-hnp-Au.** (A) Schematic illustration of the liquid flow cell. (B) Calculated and experimental plots of pressure drop versus flow speed show that the hierarchical structure of 3DP-hnp-Au reduces the pressure drop by ~10^5 times compared to np-Au. (C) Schematic illustration of the gas flow through the catalytic fixed bed reactor. GC-MS, gas chromatography–mass spectrometry. (D) Plot of reaction rate versus time that compares the gravimetric reaction rate of 3DP-hnp-Au (80 mg) and np-Au (160 mg) catalysts for methanol oxidation to form methyl formate and carbon dioxide at elevated temperature.
to be tuned without affecting the network connectivity, which dominates the strength-density dependence in np-Au with monomodal pore size distributions (37).

**DISCUSSION**

By combining 3D printing with advanced materials, we have created a new paradigm for catalyst architectures based on nanoporous materials and specifically demonstrated production of 3DP-hnp-Au with deterministic control of more than seven orders of magnitude of length scale of the structure. The hierarchical levels of structure and porosity are separately tuned by varying 3D printing, ink composition, and dealloying conditions. We demonstrated this method by developing paste-like inks with a Ag-to-Au atomic ratio of ~2:1. These inks exhibit the necessary rheological properties for printability and meet requirements for alloying/dealloying to obtain np-Au. The method described here is facile and cost-effective. 3D printing is an additive technique that enables patterning of arbitrary macro-scale form factors and complex microscale architectures without the need for expensive and time-consuming subtractive manufacturing approaches. The inks and the technology described in this work can be adapted to other extrusion-based technologies that have proven suitable for mass production. Reducing mass transport limitations and increasing reactivity, without sacrificing selectivity or stability, mean that more of the active material surface area can be used. This lowers the total requisite catalyst mass, which, in this case, is an expensive precious metal. Hierarchical control also fosters heterogeneous integration with other functional devices and testing layouts, which accelerates the design-fabricate-test innovation cycle. Furthermore, our 3D printing approach can produce compositional gradients into the structure by changing the ink composition on the fly with mixing printheads, which promises another level of structural control and possible functionality for reactor systems. We note that this approach can be adopted for other alloys, including Cu- and Ni-based alloy systems. Future work will be guided by inverse design optimization, which will focus on the development of macro- and microscale architectures for flow-through electrocatalyst electrodes for applications such as flow batteries and electrochemical carbon dioxide reduction reactions. Ultimately, the ability to control the scaling relations between volume and catalyst surface area could revolutionize the design of chemical reactors.

**MATERIALS AND METHODS**

**Ag-Au ink preparation**

Ag-Au composite inks were prepared by mixing 7 g of Ag clay [90 weight % (wt %) silver powder + 10 wt % water and organic binder; precious metal clay (PMC), Mitsubishi Materials] and 6 g of Au clay (91.7 wt % pure gold + 8.3 wt % organic binder, water, and silver; PMC, Mitsubishi Materials) with 0.5 to 1.0 g of organic solvent (PasteMaker, Sherri Haab), corresponding to an average of 70 at % Ag to 30 at % Au composition. The alloy components were mixed in a planetary centrifugal mixer (Thinky) for 1 min.

**Ink rheology**

Rheological properties of the Ag-Au composite inks were measured using a stress-controlled rheometer (AR 2000ex, TA Instruments) with a 40-mm flat-plate geometry and a gap of 500 μm. All measurements were preceded by a 1-min conditioning step at a constant shear rate of 1 s⁻¹, followed by a 10-min rest period to allow the ink microstructure to reform. A strain sweep from 10⁻³ to 10² s⁻¹ was first performed to record the apparent viscosity as a function of shear rate. A stress sweep from 10⁻² to 2 x 10³ Pa at a constant frequency of 1 Hz was also conducted to record the storage modulus and loss modulus as a function of sweep stress. The yield stress was defined as the stress where storage modulus falls to 90% of the plateau value.

**3D printing**

The composite ink was loaded into a 3-ml syringe barrel (Nordson EFD) attached by a Luer-Lok to a smooth-flow tapered nozzle [inner diameter (d), 200 μm]. An air-powered fluid dispenser (Ultimus V, Nordson EFD) provided the appropriate pressure to extrude the ink through the nozzle. The target patterns were printed using a three-axis positioning stage (ABL9000, Aerotech). The 3D Ag-Au green parts were printed onto a silicon wafer with an initial nozzle height of 0.7 d to ensure adhesion to the substrate. These printed parts were dried in the air and then thermally annealed at 850°C to form alloy structures. The typical printed sample xyz dimension was 6 mm x 6 mm x 1.6 mm, but larger parts have been printed for demonstration purposes. Using the sample weight after dealloying (60 mg), the density was calculated to be 0.9 g cm⁻³ corresponding to a porosity of 96%.

**Dealloying**

Ag was selectively dealloyed from 3D-printed Ag-Au architectures by immersion of the annealed sample in concentrated nitric acid (70 wt % HNO₃) for 48 hours. After dealloying, the samples were rinsed several times with deionized water and air-dried for 24 hours. The amount of Ag removed was determined by measuring the sample mass before and after dealloying.

**Characterization**

The dimension of the samples was determined using a caliper with an accuracy of 0.01 mm, and mass was measured using an ultramicro balance (XP24, Mettler Toledo) with an accuracy of 0.001 mg. The relative density of each specimen was calculated from the measured mass and volume. The samples were imaged with a digital optical camera and field-emission SEM (JEOL 7410) at an accelerating voltage of 5 keV and a working distance of 8 mm. The elemental composition was determined by EDS using an accelerating voltage of 10 keV. Macroscopic linear compression tests were performed using a universal testing machine (Instron 5943) equipped with a 1000-N load cell at a nominal rate of 10 μm s⁻¹. Electrochemical measurements were performed using a biologic VSP-300 potentiostat. The electrochemical surface areas of np-Au and 3DP-hnp-Au were determined by CV using the areas under the Au oxidation and reduction peaks. A potential window of 0 to 1.5 V (versus Ag/AgCl reference electrode) and a scan rate of 10 mV s⁻¹ in 0.5 M H₂SO₄ solution (American Chemical Society grade, VWR) were used. A Pt wire (0.1 mm diameter, 5 cm long) was used as the counter electrode. The specific charge equivalent of 450 μC cm⁻² was used for converting the charge associated with the gold oxide reduction to surface area, which was then divided by the sample mass to obtain the specific surface area per unit mass (33).

EIS measurements were performed in 0.5 M H₂SO₄ solution, with a frequency scan from 10 kHz to 10 mHz, and a voltage amplitude of 5 mV at a potential of 0.1 V. The solution resistance (Rₛ) was 2.55 ohms.
The charge/electron transfer resistances ($R_{ct}$) were 4.7 and 2.76 ohms for np-Au and 3DP-hnp-Au, respectively. The capacitance values were calculated from the measured imaginary component of the impedance $Z_{im}$ using the correlation $C = -1/(2\pi fZ_{im})$, where $f$ is the frequency (38). A bulk np-Au sample of the same weight, prepared by dealloying a bulk Ag70Au30 alloy, was used as a reference. The alloy was cut and rolled to a similar sample thickness with an $\chi_{xy}$ dimension of 2.0 mm × 3.0 mm × 1.6 mm. Pressure drop tests were performed in a custom-designed flow-through cell. The inlet of the cell was a diameter of 8.8 mm and was fabricated by printing four layers with a layer spacing equal to the filament diameter; the radius of the concentric circles of every other layer was adjusted to cover the spacing between the filaments within a layer, thus leaving no direct line-of-sight pathways for collisionless gas transport.

The 3DP-hnp-Au and np-Au samples were loaded into the quartz reactor tube and placed in a furnace. The catalytic test samples were activated using the previously described ozone activation procedure (39). Methanol was introduced into the reactor by bubbling He through a flask of methanol kept at room temperature. Selective oxidation of methanol to methyl formate was used as a test reaction to evaluate pressure gradient–driven mass transport through the np-metal membrane. The catalysis tests were performed in a quartz tube reactor surrounded by a furnace; the np-Au and 3DP-hnp-Au discs were loaded in the center of the reactor tube and held in place by quartz wool plugs on both sides of the discs. The reactor and discs had similar diameters to minimize bypass of the reactants. The temperature was controlled and measured with a thermocouple situated right on top of the discs. Np-Au and 3DP-hnp-Au membrane discs of the same thickness and similar diameters were prepared (optical images are shown in the insets of fig. S6). The np-Au reference sample with a unimodal pore size distribution had a diameter of 9.4 mm (same size as the inner diameter of the quartz reactor tube) and a thickness of 400 μm. The 3DP-hnp-Au sample had a diameter of 8.8 mm and was fabricated by printing four layers of concentric circles with a layer spacing equal to the filament diameter; the radius of the concentric circles of every other layer was adjusted to cover the spacing between the filaments within a layer, thus leaving no direct line-of-sight pathways for collisionless gas transport.

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