Three-dimensional conductive polymer-metal hybrid structures were engineered materials have been realized by a variety of techniques and methods, such as two-photon lithography (7) or electrodeposition (8) allowing a variety of ceramics and metals to be used in these methods. The polymer is then removed by burnout or by chemical dissolution after the structure is built up. The method uses direct printing of nanoparticle dispersions using the Aerosol Jet technology in 3D space without templating or supporting materials followed by binder removal and sintering. In addition to 3D microlattices, we have also demonstrated directly printed stretchable interconnects, spirals, and pillars. This assembly method could be implemented by a variety of microdroplet generation methods for fast and large-scale fabrication of the hierarchical materials for applications in tissue engineering, ultralight or multifunctional materials, microfluidics, and micro-optoelectronics.

INTRODUCTION

Materials with three-dimensional (3D) architectures, such as micro/nanolattices and scaffolds, are of high current interest (1) because they can exhibit extraordinary material properties and functionalities in diverse applications, such as biomedical implants (2), porous membranes (3), load-bearing structures (4), microfluidic devices (5), fast-charging and high-capacity batteries (6), and supercapacitors (7). Such microengineered materials have been realized by a variety of techniques and methods, such as two-photon lithography (4), projection microstereolithography of polymers (8, 9), and the use of a polymer opal templating (10), followed by deposition of suitable materials, such as metals or ceramics over the polymer template (4, 8, 10). The available techniques to deposit over the template (for example, atomic layer deposition, electroless deposition, or electrodeposition) allow a variety of ceramics and metals to be used in these methods. The polymer is then removed by burnout or by chemical dissolution after the structure is built up. The final product consists of hollow tubes and their composites for truss elements that form the complex 3D scaffold. Although the template fabrication and the material deposition steps are additive, the removal of the underlying template adds a fabrication step, requires the use of chemicals, and creates waste.

Free-form fabrication by printing of nanoparticle solutions and inks followed by sintering is a relatively recent area that has gained importance in the fabrication of a diverse set of electronic devices and materials (11, 12). Printing of nanoparticles over the surfaces of 3D components, such as hemispherical domes (11) or pillars (13), has been demonstrated for antenna applications. A continuous dispense of nanoparticles in the form of highly intricate microscale 3D networks, fabricated by adding silver nitrate to a photocurable oligomer in the presence of suitable photoinitiators and exposing them to a digital light system (15).

Solution-based noncontact processes (16), such as inkjet printing, have been used to print molten lead-free solder materials (17) and piezoelectric and metal nanoparticles (18, 19). Microwires or micropillars having features of the order of 100 μm were realized in these works (18, 19). Several process parameters (substrate, solvent, and droplet velocity) have also been investigated to address the fabrication constraints and requirements in the printing processes (20). Another solution-based nanoparticle printing method, namely, the Aerosol Jet technique, uses a focused sheath of gas to transfer the aerosolized microdroplets containing the nanoparticles. Such a transfer of material allows nanoparticle solutions with a viscosity of up to 1000 centipoise (cP) to be printed using this method. A wide range of feedstock materials can thus be printed; for example, inks and dispersions containing nanoparticle polymers (21), metals (13), metal oxides (22), and other ceramics (23) have been used to print using the Aerosol Jet method.

Here, we use the Aerosol Jet printing technique to deposit aerosolized microdroplets containing metal nanoparticles to assemble the nanoparticles in the form of highly intricate microscale 3D networks, such as microscaffolds/microlattices with nearly fully dense truss elements without the use of any supporting materials. The structural features are shown spanning over five orders of magnitudes in length scale. Furthermore, we were able to controllably engineer the internal porosity and surface topography of the truss elements of the scaffolds through varying sintering conditions (for example, sintering profile and/or power source), thus introducing a hierarchy in porosities within the structure, in addition to that from free-form printing.

RESULTS AND DISCUSSION

Pointwise spatial printing inspired by nature

First, we describe the free-form printing used to obtain the complex hierarchical structures described in this study. The printing process was inspired by similar methods occurring in nature that resulted in...
complex or elegant 3D architectures. For example, petal-shaped gypsum crystals typically found in the West African deserts and called “Desert Roses” are formed by precipitation and condensation of aerosolized liquid droplets (in a fog) that carry dissolved sulfur compounds. The crystal is then formed in 3D by evaporation of the solvents by the desert heat (24, 25). This process is depicted schematically in Fig. 1A. We adopted this strategy to fabricate 3D microarchitectures in a controlled manner that mimicked the natural process shown in Fig. 1A. We use silver nanoparticles dispersed in an aqueous ethylene glycol solution as a source of building material (see Materials and Methods). An aerosolized fog containing droplets from this solution is then generated from the Aerosol Jet technique and carried toward the heated substrate to build a 3D microarchitecture/microscaffold of silver nanoparticles with truss elements in the air that do not require any supporting material or templating (Fig. 1B). The principle of operation of the Aerosol Jet technique is given in section S1. We use a marked increase in the evaporation rate of the solvent droplets when their diameter is below 50 µm at moderate temperatures to solidify the deposited material (nanoparticle with binders) before the arrival of the successive droplet. A high particle loading ratio (up to about 70% by volume at the time the droplets exit the print head) is used, and the nanoparticles are sintered in the presence of an energy source, such as heat or photonic power. It is noted that this approach is independent of the microdroplet generation method, although we used the Aerosol Jet printing for finer droplet sizes and, hence, features. The achieved microarchitectures and microlattices consist of a network of interconnecting spatial truss elements at various angles to the horizontal that are as thin as 20 µm in diameter and have open void sizes ranging from 100 µm to 1 mm from the printed architectures. To achieve these fine features, precise process control is highly critical. In the next section, we present physical models to predict the required process parameters for the 3D architectures.

Physical model and control parameters

Building a 3D structure in the air with nearly fully dense truss elements without the sacrificial materials relies on accurate fabrication parameter settings, such as platen temperature and droplet loading ratio. Determination of the critical angle of growth and the stability of growing elements are the two main parameters that constrain the geometry of the 3D microscaffolds. To gain an understanding of the two parameters, we first studied the kinematics of the droplet precipitation process to predict the lowest angle of growth in space for the nanoparticle assembly for different droplet heights (measured after drying) as function of the droplet diameter (Fig. 2). The formulation of the model and the resulting equations are derived in section S2. A condensed ink droplet deposited over a ledge and the free-body diagram being considered for the analysis are shown in Fig. 2A. For spherical droplets with a radius of about 20 ± 5 µm and a dried droplet height of 10 to 20 µm, the predicted critical angle of growth is about 35° ± 7° (Fig. 2B). The second significant parameter is the solvent rate of evaporation, which dictates how fast the precipitated droplet dries out. It is desirable to have fast solvent evaporation for the nanoparticle microdroplets above the previously solidified droplet. The evaporation rate and microdroplet half-life time (that is, when the droplet loses half of its volume to evaporation) have been estimated as a function of time.

Fig. 1.Analogy of the natural growth of Desert Rose and the 3D buildup of nanoparticles by pointwise printing to realize microarchitectures. (A) An illustration of the Desert Rose formation process by condensation of sulfur-containing fog along with the elevated temperature of the desert climate. Desert Rose photo courtesy of O. Apostolidou (reprinted with permission). (B) In a process inspired by that shown in (A), we used successive condensation of droplets of nanoparticle ink in the spatial dimension followed by solvent evaporation and sintering to create controlled 3D microarchitectures with hierarchical porosity. The scanning electron microscopy (SEM) image resembles a petal-shaped structure (right). The truss element diameter is about 40 µm.
and temperature (see section S3 for the details of the derivation and Fig. 2C). It is revealed that for temperature \( \leq 100^\circ C \), the drying time increases markedly with an increase in the droplet diameter. The above-mentioned results and analyses were verified experimentally by assembling nanoparticles as pillars and successively lowering the angle of growth to find the critical angle at which the droplet would eventually fall down instead of forming the pillar, as shown in Fig. 2D. The critical angle in these experiments was about 37°, in agreement with that predicted in Fig. 2B. Further, the pillars could be realized only at temperatures higher than about 90°C, again in reasonable agreement with the prediction of the evaporation model. The models developed could thus be used to determine the required platen temperature and the stable microdroplet diameters to build a free-standing microarchitecture to fit the specific microdroplet generation method. Next, we use the method to create the unique 3D microarchitectures in two simple manufacturing steps, namely, the deposition of the nanoparticle ink droplets and final sintering.

**Three-dimensional hierarchical architectures**

Figure 3 (A to C) shows microscale networked lattice structures printed using the above schema having octahedral (Fig. 3, A and C) and hexagonal (Fig. 3B) unit cells, with fullness fractions of 27, 9.5, and 14.5% and structural periodicities of 100, 300, and 200 \( \mu m \), respectively. The overall length scale of the structures is of the order of a few millimeters. The as-printed microscale scaffolds (before sintering) consisted of nanoparticles dispersed in binders. However, after sintering, the binders are expected to escape, leaving the sintered nanoparticles to form the 3D network in space. Figure 3D shows the scaffold after sintering with the sintered nanoparticles, showing the near-full density of the truss elements. The micrographs in Fig. 3 thus demonstrate scaffold structures with high complexity at length scales described above with nearly fully dense truss elements. Next, we show that nanoparticle sintering conditions can be varied to obtain very low porosities (near-full density) to higher porosities in the truss elements if desired, which gives rise to the hierarchical structures that span over several orders of magnitudes in length scale. We note that hierarchical porosities are observed in naturally developed materials and biological systems that help them tolerate strain (26, 27). The method described in this study offers an excellent opportunity to artificially fabricate such strain-tolerant structures by tailoring porosities from nanoscales (from nanoparticle sintering) to hundreds of micrometers in scale (from the Aerosol Jet printing). For example, Fig. 3 clearly shows the
scaffold with a porosity of the order of 100 to 300 \( \mu m \) through printing in 3D. Because the truss elements are made from nanoparticles and binders when the printing occurs, different sintering conditions can remove the binders and stop the crystal growth before complete pore closure to give them variable densities. The porosities could also be manipulated by using different nanoparticle sizes.

Figure 4 shows a schematic and the micrographs of nanoparticle porosities for silver nanoparticles having diameters in the range of 30 to 50 nm. The pore sizes and length scales of the order of 100 nm are evident. We also used silver flakes of about 1 \( \mu m \) in size and sintered both types of nanoparticles under different conditions. The detailed study of the sintering conditions can be found in section S4, where different levels of porosities are observed for different sintering conditions and two particle sizes, as shown in fig. S4.

To further demonstrate the hierarchical length scales achieved by this technique, we fabricated a variety of micro-architected structures, as shown in Fig. 5. Printed silver lattices with octahedral and hexagonal architectures are shown in Fig. 5A. The truss elements have diameters in the range of 30 to 55 \( \mu m \), whereas the periodicity of pores from printing is of the order of about 300 \( \mu m \). The overall scale of the scaffold is over a few millimeters. Figure 5 (B and C) shows features at length scales of hundreds to tens of micrometers, respectively. Figure 5D...
shows a variety of microporous structures that could be achieved by sintering of nanoparticles having a characteristic length scale from several tens of nanometers to a few micrometers. The variety of motifs and the geometry of fabricated structures in Fig. 5 thus demonstrate the precision of pointwise printing in the form of controlled porous microarchitectures that span over five orders of magnitude in size scale.

**Applications of the 3D architectures**

To demonstrate the applicability of the 3D architectures fabricated in this study, we demonstrated their use as lightweight structural materials. Several microlattices with predetermined void sizes and fullness fractions were fabricated by the method described above using silver nanoparticles with sizes ranging from 30 to 50 nm. The lattices were then compressed in a universal testing machine (see section S5 for details). Figure S5C shows the results for sintered scaffold structures similar to the systems shown in Fig. 3 (A and B), with different fullness fractions and structural periodicities (dimension details are given in fig. S5, A and B, and table S2). We found that these architected materials show a high strength-to-density ratio over a wide range of densities (fig. S5) and occupy a hitherto unrealized area on the Ashby chart and could be comparable with other microlattice metamaterials (fig. SSD) (8).
The scaffold structures with hierarchical features described above represent only one of the structures that could be achieved using the proposed fabrication method. In this section, we describe other pointwise printed microstructures and devices to fully describe the use of this method. Figure 6A shows a microscaffold structure having a porous surface with 2- to 5-μm-sized voids. Such morphology is known to be highly amenable for cell proliferation and tissue bonding (28). Printed electronics and optoelectronics are current areas of interest, where stretchable spatial interconnects can be of significant use when used in flexible electronics. Figure 6B shows pointwise printed spatial microelectrodes in the form of an accordion shape made from silver nanoparticles between two commercial micro-light-emitting diodes (LEDs). The spatial geometry of these microelectrodes can provide stretchability by deformation in the third dimension. The spatial interconnects are used to control the power supply to the LED, as demonstrated in Fig. 6B. Silver microarchitectures in the form of hollow pillars with outer diameters ranging from 35 to 100 μm are shown in Fig. 6C. Such architectures can be used as heat dissipators in microelectronic devices. Figure 6D shows a high aspect ratio of spiral and thin and thick 3D interconnected truss elements from left to right. A detailed investigation of these areas can potentially lead to separate fields of study and will be part of future investigations.

Fig. 6. Demonstration of flexibility of nanoparticle buildup using pointwise printing for a wide range of applications. (A) Hierarchical porous scaffold and the topography of porous surfaces that is useful for tissue engineering and cell proliferation. (B) Stretchable spatial interconnect assembled between two micro-LEDs. Scale bars, 100 μm. (C) SEM image of array of pillars with different diameters (35 to 100 μm) and heights (85 to 500 μm). (D) (Left to right) Four spiral high aspect ratio hollow columns forming a dome show the flexibility of this method in fabrication of spatial interconnects. Fine silver interconnects with a thickness of 30 μm and an aspect ratio of over 20.
We note that the physical principles of the method described in this work can be extended to any materials that can be dispersed into a solvent-based slurry in the nanoparticle form. Further, it is possible to create composite micro-architected metamaterials by using nanoparticles of different materials in the ink or by simply changing the ink material anytime during the 3D structure formation. Further, by using heterogeneous particle sizes or different sintering temperatures that selectively allow grain growth, a random variation or a gradient in microstructure can be induced within the truss elements. Another area of future study is the determination of process parameters that affect the printing quality seen in Figs. 2, 3, 5, and 6 in terms of the agglomeration and crystallinity of the printed materials. It is interesting to note that several micropillar compression and microtorsion experiments (29, 30) show that at length scales <100 nm and ~10 μm, the material strength increases compared to that predicted from the conventional Hall-Petch relationship. Such length scales can be found in the truss elements in Figs. 3 and 5 and in the sintered nanoparticles in Fig. 5. The nanoparticle sintering and the 3D microarchitectures can thus be of high interest in this area and will also be part of a future investigation.

CONCLUSIONS
In summary, we have demonstrated a 3D microscale assembly method for nanoparticles to form self-supported complex architectures, such as scaffolds with nearly fully dense truss elements and having length scales over five orders of magnitudes. This is achieved by pointwise spatial printing of the nanoparticle solutions without the use of any templating or supporting materials. Further, by varying the postprocessing conditions, such as sintering, the porosity in the truss elements was varied. We also demonstrate the use of the hierarchical scaffolds as structural materials and that they occupy a hitherto unexplored area on the Ashby chart for the strength of the porous/cellular materials. The hierarchical 3D structures realized by this method have applications in tissue engineering, energy storage, strain-tolerant ultralight materials, microfluidic devices, and microelectronic and optoelectronic devices. This work, in addition to being an important advance in microscale bottom-up assembly of nanoparticles, bridges a length scale gap between nanoscale and microscale architectures and the macroscale device sizes required for real-world applications.

MATERIALS AND METHODS
Materials
Silver nanoparticle ink (PRELECT TPS 30, Clariant) with a density of 1.75 g/cm³, a viscosity of about 1.5 cP, a particle size of 30 to 50 nm, and a particle loading of 40 ± 2 weight % was used to form the microdroplets for the fabrication of 3D microarchitectures and mesoarchitectures. The solvents used for this ink were deionized water and ethylene glycol. Ethylene glycol acts as a humectant to help in the formation of the 3D architectures. The samples with 3D microarchitectures were fabricated on 10 × 10-mm polished alumina substrates with 96% purity (ALN-101005S1, MTI Corp.). To compare and characterize the porosity as a function of sintering conditions and particle size, we also used silver ink containing 1-μm-sized flakes (Metalon HPS-DEV 79-26-98, NovaCentrix) with 58% particle loading and a viscosity of 150 cP in the form of thin films. Note that the ink containing 1-μm-sized flakes was used only for the porosity study and not to build the 3D architectures.

Microdroplet formation and printing
The Aerosol Jet printer (AJ300, Optomec Inc.) was used to aerosolize the nanoparticle ink. Before printing the structures, the ink material was placed in a tube, which was rotated continuously around its axis for a minimum of 12 hours using a tube roller (MX-T6-S, SCILOGEX) at about 70 rpm to prevent nanoparticle agglomeration within the ink. The silver nanoparticle ink with particle size of 30 to 50 nm was mixed with deionized water at a volume ratio of 3:1 before the atomization process inside the AJ300 machine. An ultrasonic atomizer was used to create the aerosol/mist. The nozzle exit diameter during printing was 100, 150, or 200 μm, depending on the desired truss element diameter. Note that the beam of the aerosol particles was focused to about 10 times smaller in diameter because of the sheath gas when compared to the nozzle diameter according to the manufacturer’s observation.

Measurement of droplet properties
The contact angle measurement was done using a goniometer (VCA Optima and PDASt software, AST Products Inc.). The nanoparticle ink was first dispensed on an alumina substrate to form a 3-mm × 3-mm pad using the Aerosol Jet machine and dried at 80°C for 24 hours. The density of the nanoparticle ink coming out of the nozzle was determined by measuring its volume at a 1-μl accuracy (Hamilton, 81020 1710TTL) and by weighing it in a microbalance (AT201, Mettler-Toledo) at a 0.01-mg accuracy. The density of the droplets exiting the Aerosol Jet nozzle after atomization was determined to be about 6500 ± 500 kg/m³ for five readings. Further, a sample of concentrated ink with the same density was prepared from the original ink by providing slow solvent evaporation at 60°C and continuous stirring. The concentrated ink droplet was then dispensed onto the previously printed and dried pad, and the contact angle was immediately measured on 10 samples after dispense. The measured contact angle (θ) was 85°. We recognize that the waiting time between dispense and measurement can affect the contact angle as the evaporation proceeds, and this was not considered in the present analysis. The γSL was measured using the pendant method, along with real-time video analysis with 60 frames/s (VCA Optima and PDASt software, AST Products Inc.). The γSL was determined to be 7.8 ± 4.4 J/m² for 12 readings.
Sintering conditions
To fabricate the 3D microlattices and mesolattices in Figs. 1 to 3, we sintered the samples at 200°C for 30 min in a programmable oven (Neytech Vulcan furnace, model 3-550, Degussa-Ney Dental Inc.). The heating rate was set at 40°C/min. For Fig. 5D (left), the photonic sintering was done using a Xenon Sinteron 2000 (Xenon Corp.) at an energy setting of about 3 J/cm² on the equipment. The heating rate and sintering conditions for the experiments used to study the void formation are given in section S4.

SUPPLEMENTARY MATERIALS
Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/3/e1601986/DC1

section S1. Aerosol Jet printing technique
section S2. Physical model for the critical angle of growth
section S3. Droplet evaporation rate
section S4. Voids/porosity as a function of the sintering conditions
section S5. Compression tests
fig. S1. An illustration of the Aerosol Jet printing technique.
fig. S2. Schematic of pointwise printing process.
fig. S3. A droplet at the edge of supporting plane.
fig. S4. Porosity evolution for two different particle sizes and sintering conditions.
fig. S5. Mechanical behavior of the 3D-printed hierarchical scaffolds fabricated by the pointwise printing method.
table S1. Properties of ethylene glycol, the solvent used for the nanoparticle ink.
table S2. Information about compression test samples and test results.
movie S1. Video showing compressive loading of a 3D microlattice fabricated by the pointwise printing method.

REFERENCES AND NOTES
8. X. Zheng, H. Lee, T. H. Weisgraber, M. Shusteff, M. S. Saleh, C. Hu, R. Panat, Three-dimensional microarchitected materials and preparing and editing the manuscript. C.H. carried out the sintering porosity study. All authors contributed to interpreting the data.

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