Three-dimensional (3D) microarchitected materials are important to a wide range of emerging technological applications. We report a method to synthesize complex 3D microengineered materials, such as microlattices, with nearly fully dense truss elements with a minimum diameter of approximately 20 μm and having high aspect ratios (up to 20:1) without using any templating or supporting materials. By varying the postprocessing conditions, we have also introduced an additional control over the internal porosity of the truss elements to demonstrate a hierarchical porous structure with an overall void size and feature size control of over five orders of magnitudes in length scale. 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.
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 $37^\circ$, in agreement with that predicted in Fig. 2B. Further, the pillars could be realized only at temperatures higher than about $90^\circ C$, 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 μm 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 μm 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 μm, whereas the periodicity of pores from printing is of the order of about 300 μm. 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

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Fig. 3. **Pointwise-printed 3D microarchitectures with different network topologies.** (A) An open octahedral microarchitecture with truss elements having a diameter of about 35 μm. Scale bars, 50 μm. (B) Pointwise-fabricated microarchitecture with a combination of octahedral and hexagonal structures. Scale bars, 50 μm. (C) Top surface of an octahedral scaffold structure at different magnifications and (D) truss elements of the 3D-printed scaffold after binder escape and nanoparticle sintering and possible grain growth.

Fig. 4. **The pointwise printing in combination with controlled sintering technique.** The printed material is designed to contain the first level of macroporosities. Coalescence of sintered nanoparticles starts to form the second level of porosity and could be stopped before pore closure and grain growth. Scale bars, 100 nm.
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. S5D) (8).

![Fig. 5. Pointwise-printed hierarchical materials with 3D microarchitectures having features that span over five orders of magnitudes in length scale.](http://advances.sciencemag.org/)

(A) SEM images of octahedral and hexagonal microlattices at a bulk view at a length scale of millimeters. (B) High aspect ratio truss elements forming the architecture of sintered structures introducing the first level of porosity. (C) The engineered surface of truss elements of the lattice induced by different sintering profiles featuring a high level of porosity to near dense materials. (D) The final order of controlled surface features and porosity for different sintering temperature profiles that show several microscale to nanoscale voids.
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 <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 magnitude. This is achieved by pointwise spatial printing of the nanoparticle solutions without the use of any templating or supporting materials. Further, by varying the post-processing 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 micro-electronic 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 microarchitecture were fabricated on 10 × 10-mm polished alumina substrates with 96% purity (ALN-10100551, 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. The time required to print the scaffold structure varied depending on the platen temperature, the nozzle size, and the structure complexity. For example, the time required to build the scaffold structures similar to that shown in Fig. 3A for a print head was of the order of 40 min. For the printing process, the atomizing flow rate and the sheath gas flow rates were maintained at 28 and 40 sccm (standard cubic centimeter per minute), respectively, which could be slightly altered to achieve the desired printing quality. The platen temperature was set in the range of 90° to 110°C. During printing, the standoff distance between the substrate and the nozzle was kept at about 3 mm and elevated manually every 50°μm of structure growth to avoid physical contact between the nozzle and built structure and to keep the structure in the camera’s field of view. The droplet diameter after precipitation was measured using an optical camera (FL3-GE-152C, Point Grey). The fullness fractions (volume %) of the samples were estimated using the truss diameters from the SEM images and the total scaffold-lattice structure and were expected to be within ±1%. The fullness fraction does not consider the second-order hierarchical void percentage within the truss elements and is, hence, conservative. The principle of operation of the Aerosol Jet technique is given in section S1.

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 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

REFERENCES AND NOTES

References (31–36)

Three-dimensional microarchitected materials and devices using nanoparticle assembly by pointwise spatial printing
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