Additive-Free, Gelled Nanoinks as a 3D Printing Toolbox for Hierarchically Structured Bulk Aerogels

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Aerogels are highly porous solids that maintain the properties of individual nanomaterials at a macroscopic scale. However, the inability to fabricate hierarchical architectures limits technological implementation in energy storage, gas-sorption, or catalysis. A 3D-printing methodology for additive-free TiO₂ nanoparticle-based aerogels is presented with full control of the nano-, micro-, and macroscopic length-scales. To compensate for ink's low solid loading of 4.0 vol% and to enable subsequent processing into aerogels via supercritical drying, the printing is done in a liquid bath of alkaline pH. The 3D-printing protocol retains a high specific surface area of 539 m² g⁻¹ and a mesopore diameter of 20 nm of conventionally casted aerogels while offering an unparalleled designability on the micrometer scale. To illustrate the new geometric freedom of 3D-printed aerogels, the microstructure of a strongly light-absorbing, photothermal Au-nanorod/TiO₂ aerogel is defined. To date, photothermal nanomaterials are mainly applied in the form of unstructured films where scalability is limited by light attenuation. Microstructures in 3D enhance light penetration by a factor of four and facilitate spatially defined heating on a macroscopic scale. The process can be generalized for a broad material library and allows to design inks with specific functionality, thus making aerogels adaptable for their target application.

1. Introduction

Nowadays, colloidal nanochemistry can provide well-defined nanomaterials of various sizes, shapes, compositions, and surface chemistry with remarkable properties on a large scale.¹ However, the high-volume manufacturing of macroscopic, nanomaterial-based devices is still challenging. The main difficulty of nanomaterial processing is the preservation of nanoscopic properties across multiple length scales.² An attractive approach to bridge the nanoscopic and macroscopic world is to process nanomaterials into aerogels via gel casting.³,⁴ This method translates the intrinsic properties of nanoparticle dispersions into highly porous bulk solids with immense surface area. However, the restricted range of mold geometries and aerogel's poor subtractive processing abilities limit shape tunability and prevent complex microstructured geometries.

A promising technology that could enable free-form fabrication of nanoparticle-based aerogels is the use of direct ink writing (DIW), a subcategory of extrusion-based 3D printing. DIW evolved from ceramic processing which similarly to nanoparticle-based aerogels fabricate materials and devices from preformed particles.²,⁵ Nevertheless, ceramics and nanoparticle-based aerogels have fundamentally distinct properties defined by large differences in the particle size of the primary building blocks and the porosity of the final product. Nanoparticle-based aerogels feature porosities of up to 99.8% and preserve the outstanding properties of the individual, nanometer-sized particles in a nanostructured macroscopic solid.³,⁶ In contrast, ceramics are dense solids,
where size-specific properties of the individual particles are lost upon sintering. Thus, to enable optimal processing into dense, mechanically stable solids, particles are typically larger than 100 nm.\[2,7\] The low porosity of ceramics implies that highly concentrated inks can be printed to obtain objects that marginally shrink upon drying in air.\[8\] In contrast, solvent evaporation is still a major challenge for DIW of highly porous aerogel materials.\[9\] To compensate, recent studies formulated inks based on high boiling point solvents.\[10\] However, these inks rely on high volumetric loadings of preformed aerogel microparticles which are bound by polymers to ensure their printability. These recipes drastically differ from gelation protocols of conventionally casted nanoparticle-based aerogels which do not require any rheological additives or preformed aerogel microparticles.\[3d\] While organic residues degrade the performance as a catalyst or thermal insulator by blocking active sites or compromising aerogel’s exceptional low thermal conductivity,\[10b,11\] the use of 10 μm aerogel particles results in grain boundaries and impedes a true bottom-up fabrication with full control of the nano-, micro-, and macroscopic length scales.\[10a\] Thus, to fully exploit intrinsic or even synergistic properties of nanomaterials in a 3D printed aerogel, additive-free inks similar to conventionally casted aerogels need to be formulated.

In this study, we close the gap and report a 3D printing process for the fabrication of TiO$_2$-based aerogels. We formulate additive-free inks of gelled TiO$_2$ nanoparticles with a volumetric loading of 4 vol%. Instead of using rheologic additives, we compensate for the low particle concentration by printing in a liquid bath of alkaline pH. This allows us to maintain the ink’s nanoscopic characteristic and to fabricate macroscopic translucent aerogel geometries. Moreover, we demonstrate that multi-component inks can be easily processed by mixing TiO$_2$ with additional nanoparticle dispersions such as spherical Au nanoparticles (AuNP) or Au nanorods (AuNR) prior gelation.

To demonstrate the design flexibility of our method, we print various geometries with high shape fidelity and precision, including void-free cubes, 3D grids, boats with large overhangs, and various multi-material geometries. The 3D printed aerogels inherently feature a randomly organized interconnected mesoporous network with pore sizes in the range of 20 nm, a large specific surface area of up to 539 m$^2$ g$^{-1}$, and a low density of 0.2 g cm$^{-3}$—typical values for conventionally cast metal oxide aerogels.

To give a first glimpse of the new design freedom for 3D printed nanoparticle aerogels, we combine the superior thermal insulating capabilities of metal-oxide aerogels with photothermal properties of plasmonic AuNRs. Here, the 3D printing process defines not only the dimension of the printed material but also the material composition and photothermal properties at any desired spot. Finally, we engineer the microstructure of the photothermal aerogel for improved light penetration and more homogeneous heating in 3D. This enables a new generation of photothermal devices for solar steam generation or thermochemical heat storage.

2. Results and Discussion

Figure 1a provides an overview of the 3D printing process developed in this work which consists of three steps: i) ink formulation by nanoparticle gelation, ii) 3D printing in a liquid bath, and iii) post-processing via supercritical drying. Key challenges are formulating a printable, additive-free ink of low solid loading and designing a process that maintains the nanoscopic characteristics of gelled nanoparticles in a macroscopic, 3D printed aerogel. Having solved these problems, geometries of various complexity and material composition can be fabricated as indicated in Figure 1b–g.
2.1. Ink Formulation

We have synthesized ligand-free 4 nm anatase TiO₂ nanoparticles by adopting a synthesis described elsewhere.[12] For ink formulation we transformed the liquid dispersion into a volume-filling nanoparticle gel, as illustrated in Figure 1a. To this end, we destabilize the TiO₂ dispersion in a controlled manner and crosslink the nanoparticles by a subsequent thermal treatment. Unlike previous reports, where selective ligand removal has been used for destabilization,[3b,6b,13] we modify the force balance of electrostatically stabilized TiO₂ nanoparticles. The range of electrostatic forces can be described by the Debye length where high values increase colloidal stability.[3d] The addition of solvents with lower dielectric constants such as acetonitrile reduces the Debye length and causes an overall net attraction between particles. For optimal results we dilute the aqueous dispersion to one-third with acetonitrile. Acetonitrile contents of 50% or higher cause precipitation, whereas the absence of acetonitrile prohibits gelation, as illustrated in Figure S1, Supporting Information.

Previous inks for 3D printing of aerogels were gelled by increasing the attractive hydrogen bonding via the addition of additives.[10b,14] We would like to point out that such inks are special recipes to enable 3D printing of aerogels and feature a different chemical composition than recipes for conventionally casted aerogel materials. In our approach, we stick to the well-established concept for casted nanoparticle-aerogels which consists of the two steps: 1) Preparation of stable nanoparticle dispersions and 2) gelation via controlled destabilization.[3a,c,d] Thus, all intriguing properties of casted nanoparticle-aerogels will remain in a 3D printable ink.

Ultimately, 3D printing relies on extrusion of microscopic filaments; high particle loadings facilitate filament extrusion, but reduce the porosity of the final aerogel. To estimate the minimum concentration for 3D printing, we gelled inks with TiO₂ loadings of 0.2, 1.2, and 4.0 vol% and checked the optical appearance upon extrusion through a 410 µm nozzle in Figure 2a–c. Figure 2c demonstrates successful filament formation for a 4.0 vol% ink, but further rheological criteria need to be fulfilled for good printability. Suitable inks must possess high viscosity and paste or gel-like characteristics at rest, but also feature a low viscosity and fluid-like character while passing through thin deposition nozzles.[15] Besides, the ink must rapidly transform from a fluid-like into a solid-like material after leaving the nozzle to
preserve the shape of the extruded filament—especially when spanning gaps in the underneath layer. We assess the rheological fingerprint of each ink by shear rheology. To replicate the flow characteristic of each ink at rest and while printing, we investigate the apparent viscosity as a function of shear rate in Figure 2d. We demonstrate a profound shear-thinning behavior. Thus, during extrusion the flow resistance is drastically reduced for typical shear rates of 10–150 s⁻¹,[17] whereas at rest the ink has a low tendency to spread. Further, we clarify the microstructure of gelled inks via oscillatory frequency sweeps shown in Figure 2e. Here, the elastic modulus G’ and viscous modulus G” are plotted as a function of time for a frequency range of 1–50 Hz. G’ and G” are nearly frequency-independent for a particle concentration of 4.0 vol%. Thus, we conclude that an elastic, solid-like network has formed.[18]

The mechanical stability of the ink is defined via the interaction of particles within the gelled network. As soon as the applied shear stress exceeds the yield stress τy, the connection between individual particles or larger clusters starts to break apart.[19] When the shear stress overcomes the flow stress τf, a sufficient number of bonds in the particle network are disrupted and the ink eventually flows with a shear-thinning behavior. We estimate τy and τf based on oscillatory amplitude sweeps shown in Figure 2f, which is a plot of G’ and G” versus the stress amplitude. Here, τf is taken as the stress required for a 90% decrease of the initial elastic modulus G’0 and τy is defined as the crossover between G’ and G” at low stresses the ink shows characteristics of an elastic solid since G’ is larger than G” at higher stresses G” slowly decreases until it sharply drops and eventually approaches values lower than G’; thus representing a viscous fluid. For a particle concentration of 4.0 vol% we determine τy and τf as 104 Pa and 210 Pa, respectively.

After leaving the nozzle, the flowing ink needs to rapidly regain a gel-like attribute to preserve its shape. To track this recovery, we performed an oscillatory recovery test shown in Figure 2g. Here, the 4.0 vol% sample instantly recovers a solid-like characteristic (G’ > G”) as soon as the oscillation amplitude changes from a high to a low value mimicking the transition from high to low shear stress once the ink exits the nozzle during 3D printing.

In summary, the ink with a particle concentration of 4.0 vol% is not only best suited for 3D printing based on the ability to reliably form filaments, but also due to a distinct shear-thinning behavior, a pronounced gel-character at rest, and an immediate gel recovery after extrusion. These properties are simply achieved by careful control of solvent composition and particle concentration without the need of any rheologic additives. In comparison, inks with lower particle loadings display strong frequency dependency of G’ and G” and feature lower τy and τf as shown in Figure 2e and f, respectively. Thus, these inks represent characteristics of a viscoelastic fluid that tends to form droplets instead of filaments during extrusion. Moreover, multi-component inks can directly be obtained by performing TiO2 gelation in the presence of other nanomaterials such as AuNPs or AuNRs, as long as the rheologic properties of neat TiO2 are preserved, as shown in Figure S2, Supporting Information for Au loadings of up to 0.49 wt%. We expect that rheological properties of inks will change more drastically when much higher loadings of AuNPs or AuNRs are present. Thus, the rheological properties of the ink would have to be adjusted by tuning the temperature and duration of the thermal treatment or by adjusting the volumetric ratio of water and acetonitrile.

2.2. 3D Printing of Stable Complex Structures—A Force Balance Approach

We use optimized inks with TiO2 loading of 4.0 vol% to design a 3D printing scheme that enables processing into aerogels. This step requires well-controlled drying of the wet gel to preserve the 3D nanoparticle framework. When dried in air, capillary forces at the liquid/gas interfaces lead to drastic shrinkage and the nanoporous network eventually collapses. The most common drying method for casted aerogels is supercritical drying where a liquid/gas interface no longer exists, and stress is minimized.[60] However, 3D printing is typically performed in air and extruded filaments quickly dry based on their high surface-to-volume ratio. Thus, a filament of the gelled ink turns opaque within seconds of extrusion in air, as shown in Figure 3a, and eventually collapses. We overcome evaporation-induced gel damage by performing the 3D print in a liquid bath.[84,17,21] Buoyancy force necessitates that the density of the bath is significantly lower than the density of the ink. Moreover, ink adhesion demands that the substrate is preferentially wetted by the ink and not by the bath. Alkanes such as n-heptane fulfill both requirements.

Figure 3 shows an optical micrograph time series of a grid geometry printed in n-heptane. While printing in n-heptane is possible, severe post printing deformation takes place on a time scale of 24 h. Printing in a liquid bath suppresses solvent evaporation, however the ink remains soft and is still able to deform. Based on the shape evolution of the printed geometry in Figure 3b–d we identify gravity and capillary pressure as primary external forces acting on the print. To compensate adjustments on the 3D printing process need to be made. To this end, we identify the main driving force of deformation and estimate the contribution of each component. For sagging, the weight of the entire geometry needs to surpass the yield stress τy of the lowest layer. As illustrated in Figure 3e each layer of the grid geometry consists of an array of filaments of diameter d and spacing h. Due to a periodicity of h, the filament in the lower layer (colored in red) only needs to carry a small section of filament in the layer above (colored in blue). The gravitational pull of this section is defined via the weight mink, volume Vink and density ρink as mink g = ρink (πd²h/4) g. The gravitational pull of this filament segment is partly compensated by the buoyancy forces of the liquid bath. The resulting net force is distributed over the filament’s interfacial area d² and causes a gravitational pressure of pgrav = g mink (ρbath − ρink)/4. Multiplying the gravitational pressure of a single layer pg with the number of layers yields the total gravitational pressure Pgrav onto the first layer. Consequently, the weight of the geometry shown in Figure 3b imposes a gravitational pressure Pgrav of 32 Pa and gravity is therefore excluded as the main driving force of deformation (Pgrav < τy). However, according to the Young-Laplace equation (∆p = 2γ/r) a capillary pressure of 320 Pa can be approximated by taking the filament radius of r = d/2 = 125 μm and interfacial tension of γ = 20.0 mN m⁻¹ (Figure S3, Supporting Information) into account. Therefore, even a single pending filament with negligible gravitational

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pressure tries to reduce its total curvature and interfacial energy by forming a droplet at the tip as shown in Figure S3, Supporting Information. Hence, capillary pressure can be defined as the main driving force of print deformation ($\Delta p > \tau$).

In principle, capillary pressure driven deformation can be lowered by either employing surfactants for a reduced bath-ink interfacial tension or by increasing TiO$_2$ concentration for a higher yield stress. In practice, both turned out to be insufficient as discussed in the Supporting Information. Instead, we have developed a condensation process, which significantly increases the yield stress of the ink after extrusion. Although TiO$_2$ particles are pre-gelled during ink formulation, the gel network is not fully developed and TiO$_2$ particles are still able to crosslink via condensation reactions. The condensation rate can be precisely controlled via pH. While an acidic pH induces a slow condensation, which is ideal to formulate a pre-gelled ink with suitable rheologic properties, alkaline conditions significantly accelerate condensation.[22] We exploit the change of condensation reaction rates to strengthen the particle network after extrusion. For this purpose, we additionally load the heptane bath with NH$_3$. As soon as the NH$_3$ diffuses into the aqueous ink, NH$_4^+$ deprotonates a small fraction of the water to yield ammonium and hydroxide ions. As a result, the pH of the ink rises and the printed microgrid which eventually formed a droplet in a heptane bath within 24 h fully remained its 3D architecture in heptane/NH$_3$ (Figure 3f–h). Here, the pH assisted condensation is verified by a color change of the loaded pH indicator from red to yellow. Similarly, a pendant TiO$_2$ filament shows no apparent deformation as illustrated in Figure S3, Supporting Information. Thus, the role of our heptane/NH$_3$ bath is twofold and goes beyond other liquid bath approaches where the liquid is only used to prevent solvent evaporation during 3D printing.[17,21] In our approach, the liquid is charged with NH$_3$ to solidify the ink via pH-induced condensation reactions which counters deformation by external forces. In other approaches, deformation by external forces was balanced by performing the print in soft supporting materials such as polydimethylsiloxane (PDMS), laponite, or carbopol.[23] However, prints either remain embedded in the viscoelastic PDMS matrix or cannot be removed as easily as for the liquid heptane/NH$_3$ bath used within this work.

After condensation, the solvent within the gel is still a H$_2$O/acetonitrile mixture as defined during ink formulation. To enable processing into aerogels via solvent exchange and supercritical CO$_2$ drying, the printed geometries need to be removed from the heptane/NH$_3$ bath. For this purpose, prints are performed on polymer coated silicon substrates. The polymer coating is needed for reliable removal of the print from the silicon substrate and consists of a polyanlypyrrolidone (PVP)/poly(methylmethacrylate) (PMMA) bilayer. PVP is soluble in water. Thus, it easily dissolves when transferring the substrate from the heptane/NH$_3$ bath to a water/acetonitrile mixture. In this step the PMMA layer and printed gel detach from the silicon substrate, as illustrated in Figure S4c, Supporting Information. Moreover, heptane residues that are still attached to the gel automatically rise to the surface due to its lower density. The PMMA layer is dissolved during the subsequent solvent exchange to acetonitrile which in any case is necessary to enable solvent removal via CO$_2$ supercritical drying.

External forces affect the gelled ink not only after but also during extrusion. Figure 4a illustrates that a two-zone flow pattern arises when the ink passes through a nozzle. Based on the radially varying shear stress $\tau(r)$ profile, plug flow of a gel core occurs at lower shear stress in the inner part of the nozzle, whereas laminar flow of a fluid shell develops at stresses larger than $\tau_c$.[17,24] In the Supporting Information we estimate a fluid-like characteristic for $\approx76\%$ of the filament's cross-sectional area. After leaving the nozzle, the fluid shell regains a gel

Figure 3. Experimental obstacles for DIW of TiO$_2$ nanoparticle-based aerogels. a) Optical micrograph timeseries of a pending TiO$_2$ gel filament after extrusion through a nozzle with inner diameter of 410 µm in air. Optical micrograph timeseries of a microgrid 0, 12, and 24 h after printing in b–d) heptane and e–h) heptane charged with NH$_3$, respectively. e) Schematic representation of a microgrid printed with a nozzle of diameter $d = 2r$ and filament center-to-center distance of $h$. Despite (a) all inks are loaded with a pH indicator to illustrate the pH induced condensation of the TiO$_2$ gel. The microgrids in (b,f) were printed with a 250 µm nozzle and consist of 23 layers where each layer is an array of parallel filaments with a center-to-center distance $h$ of 500 µm. Consecutive layers are normally oriented to each other.
characteristic within a fraction of a second (Figure 2g). We take advantage of the intermediate fluid shell to affect the internal structure of printed parts. When printed in a microstructured geometry, the ink easily fuses with the layer underneath for excellent layer adhesion as shown in Figure 4b. When printed in an unstructured geometry, filaments fuse into a compact, void-free object as verified by X-ray microtomography and cross-sectional scanning electron microscopy (SEM) images in Figure 4d,e, respectively. For both geometries, the ink needs to fulfill two contradictory requirements. The microstructured architecture demands an ink with high mechanical stability that bridges gaps in the layer underneath and does not spread after extrusion, whereas the compact, void-free geometry requires a soft ink that easily flows to merge into continuous layers. In our approach, we satisfy both criteria with a single ink by combining shear forces during extrusion with a subsequent stabilization of the soft ink in an alkaline liquid bath. Further mechanical characterization in Figures S5 and S6, Supporting Information indicate that 3D printed samples remain stable even when loaded with the 645-fold of the own weight or when trying to peel of layers with adhesive tape, respectively.

Combining inks of gelled nanoparticles with a macroscopic fabrication technique bridges multiple length scales at once. For illustration, we printed a grid architecture with lateral dimension of 1.3 cm and highlight the macro-, micro-, and nanoscopic length scales in Figure 5. Here, the microscopic features are defined by the nozzle diameter. The print in Figure 5 was performed with a 250 µm nozzle, but nozzle sizes in a range of 150 to 1540 µm were successfully tested throughout this study. Due to the nanoscopic particle size of our ink’s components, we expect that even finer nozzles diameters can be used without causing any clogging. Optical and SEM images in Figure 5a-c demonstrate that the macroscopic geometry consists of individual filaments with a diameter of ≈200 µm, which indicates shrinkage to ≈80% of the initial nozzle diameter. We observed similar values for casted aerogels. Shrinkage mainly occurred during solvent exchange, partly during CO2 supercritical drying, and could be minimized by extending the gel aging periods.[25] A SEM image of the filament surface in Figure 5d shows a homogeneous porous network over the whole area displayed. A closer look via high magnification SEM and TEM images in Figure 5e,f reveals a delicate, continuous 3D pore

Figure 4. Illustration of shear-induced fluid-shell formation and impact on filament’s interface in a microstructured and an unstructured, compact geometry. a) Based on the radial dependence of shear stress within the nozzle, a two-zone flow pattern evolves where a gel core is surrounded by a fluid shell. b) Schematic representation of a microstructured geometry and SEM close-up of a 3D printed sample. Due to fluid-shell, filaments easily fuse with the layer underneath. c) Illustration of the expected internal structure for a compact geometry in absence and presence of a fluid-shell. d) X-ray microtomography and e) SEM cross-sectional images reveal that no voids are present within a compact geometry, underlying fluid-shell character of our ink. Additional tomographic reconstructions of a microstructured and compact geometry are shown in Video S1, Supporting Information.
network consisting of individually crosslinked TiO$_2$ nanoparticles with an original particle size of $\approx 4$ nm.

For further quantification of the pore network we performed nitrogen physisorption measurements. Nitrogen isotherms and pore size distributions in Figure S7, Supporting Information reveal that a 3D printed and casted aerogels feature a mean pore size of 20 nm and specific surface areas of 539 and 489 m$^2$ g$^{-1}$, respectively. Besides, a total porosity of 95% can be approximated for both samples by taking the bulk density of anatase (3.9 g cm$^{-3}$) and the density of the aerogel samples (0.20 g cm$^{-3}$) into account. We conclude that the mesoporous structure of the aerogel is fully preserved and not affected by the 3D printing process.

2.3. Photothermal Properties in 3D

The use of two print heads loaded with different nanomaterials expands our 3D printing approach to multimaterial geometries. As an example, we formulate inks with distinct optical properties. TiO$_2$ ink only absorbs UV radiation and appears translucent, whereas an TiO$_2$ ink loaded with AuNRs features strong extinction in the visible- and near-infrared range due to plasmonic excitations. We join both inks and print letters with the AuNR loaded ink on top of pure TiO$_2$ plates. Figures 6a,b demonstrate that TiO$_2$ preserves a translucent character upon supercritical drying, whereas the AuNR/TiO$_2$ gel changes color from reddish to green. UV/Vis spectra in Figure 6c confirm that both plasmonic peaks of AuNRs remain during the drying process, but that the longitudinal peak blue shifts by 144 nm. Since AuNRs are homogeneously dispersed in the TiO$_2$ aerogel matrix, as verified by high-angle annular dark field scanning transmission electron microscopy images in Figure S8, Supporting Information, we attribute this color change to a change of the AuNR’s dielectric environment upon removal of the solvent from the wet gel.$^{[26]}$

We utilize AuNR’s strong light extinction coefficient and free-form fabrication capabilities of 3D printing to locally define photothermal properties. As illustrated in Figure 6d–g, structured aerogels are selectively heated up to 47 °C upon illumination with a 300 W Xe light source.

Furthermore, with three selected examples we demonstrate how 3D structuring improves light-matter interaction. As a benchmark we printed an unstructured AuNR/TiO$_2$ block of $7 \times 7 \times 4$ mm that can also be fabricated via conventional gel casting techniques. We measure the temperature increase $\Delta T$ with an IR camera upon illumination with a 300 W Xe light source as illustrated in Figure 7a. We observe a rapid temperature increase of up to 62 °C (absolute 89 °C) for the light facing surface, as displayed in Figure 7b. Moreover, after illumination is stopped temperature drops sharply and continues into a longer tail until all thermal energy is dissipated, similar to previously reported plasmonic nanoheaters.$^{[26,27]}$ Besides, neat TiO$_2$ aerogel does not show significant heat generation under same experimental conditions due to the absence of AuNR as verified in Figure S9, Supporting Information. The nanoporous TiO$_2$ framework not only aids as structural support for AuNR, but also provides an excellent heat insulating environment with thermal conductivities similar to air.$^{[6a,26]}$ While this enables rapid heat generation upon illumination, high temperatures are limited to the light facing surface and drop strongly with increasing sample thickness, as illustrated in Figure 7a.

To expand photothermal heating from a thin layer to a 3D object, we improve light penetration by designing two microstructured grid geometries as shown in Figure 7c.
grids, each layer consists of an array of parallel filaments and alternating layers are orientated 90° to each other. Consecutive layers of same orientation are aligned without any shift or shifted by half of the filament separation distance. We call these geometries ‘aligned’ and “shifted,” respectively. For an unstructured block, light intensity drops exponentially as determined by the material’s extinction coefficient. For microstructured geometries, light extinction decreases because of an increase in porosity. Moreover, for similar porosity, maximum light penetration is expected for the “shifted” geometry due to the absence of a direct line of sight.

Figure 7d compares the temperature distribution as a function of sample thickness for all geometries. We observe that temperature decays strongest for the unstructured geometry and less for the microstructured geometries. For a penetration depth of \( \approx 7 \) mm, we measure a six times higher temperature increase \( \Delta T \) of 18 and 3 °C for the shifted and unstructured geometry, respectively. To further quantify the light penetration improvement for the microstructured geometries, we first derive an attenuation coefficient for the AuNR/TiO\(_2\) aerogel by fitting the temperature profile of the unstructured block with an exponential function. In a next step, we relate the coefficient to the temperature distribution of both grid geometries. For the aligned geometry, the temperature decay is well described with about half of the block’s value \( 1/2 \sigma_{\text{block}} \)—corresponding well with light absorption in every second layer of a freestanding filament. The temperature decay of the shifted geometry drops half as much as for the aligned grid and thus follows a quarter of block’s attenuation coefficient \( 1/4 \sigma_{\text{block}} \). Consequently, microstructuring in 3D enables spatially tunable light harvesting on a macroscopic scale as reflected by a more homogeneous temperature distribution within the sample.

3. Conclusion

We demonstrate a strategy for additive manufacturing of TiO\(_2\) nanoparticle-based aerogels. Unlike typical 3D printing protocols, we do not incorporate any rheologic modifiers or non-volatile solvents to compensate for the low solid loading of gelled inks. Instead, we print in an alkaline liquid bath that prevents premature solvent evaporation and increases mechanical stability of the additive-free ink during 3D printing. Thus, the beauty of our approach lies in the fact that inks of low solid loadings can be made printable without affecting the nanoscopic properties of conventionally casted aerogels. As a result, we are able to structure aerogels on seven orders of magnitude in single or multimaterial architectures of arbitrary complexity. Our strategy of printing in a liquid bath charged with a gelation agent can be applied to other colloidal chemistries than TiO\(_2\). The as reported approach of pH assisted condensation in a heptane/NH\(_3\) bath should be easily applied to other metal oxides.
aerogels such as SiO$_2$, Al$_2$O$_3$, or ZrO$_2$ due to their similar surface chemistry. Moreover, the strategy should also be universally applicable to other material classes such as noble metal aerogels by replacing the NH$_3$ with a corresponding gelation agent.

To illustrate the new fabrication freedom of 3D printed nanoparticle-based aerogels, we spatially control the photothermal functionality of plasmonic AuNRs. In the past, photothermal heating of plasmonic nanoparticles was already exploited in several prototypes for clean water regeneration, triboelectric energy generation, or photothermal catalysis.[26–28] However, due to the inability to structure nanoscopic properties on a 3D macroscopic scale, postulated devices mainly consist of thin films where heating is limited to the surface and scalability needs to be improved. We show for three selected geometries that 3D structuring improves light penetration by a factor of four—thus enabling a more homogenous heat generation in a macroscopic object. Moreover, we demonstrate that 3D printing of inks with different photothermal activity allows to restrict heating to locally defined spots.

Ultimately, our 3D printing approach offers a completely new approach to engineer large scale 3D structured architectures with a significantly lower areal footprint than already reported thin-films. As applications of nanoparticle-based aerogels go well beyond photothermal devices, this work presents a versatile method for fabricating macroscopic aerogels of determined geometry and functionality.

4. Experimental Section

Materials: Acetonitrile (99.95%), diethyl ether (≥ 99.9%), ethanol (EtOH, anhydrous, ≥ 99.9%) were purchased from VWR. Ammonium hydroxide solution (28.0–30.0% NH$_3$ basis), benzyl alcohol (anhydrous, 99.8%), gold(III) chloride trihydrate (>99.9%), L-ascorbic acid (99.5%), methyl orange, poly(methyl methacrylate) (PMMA, average $M_w = 120$ 000), poly(vinylpyrrolidone) (PVP, average $M_w = 40$ 000),...
silver nitrate (AgNO₃, ≥99.0%), sodium borohydride (NaBH₄, 99%), sodium citrate tribasic dihydrate (≥99.0%), titanium(iv) tetrachloride (TiCl₄, 99.9% trace metal basis) were purchased from Sigma Aldrich. Cetyltrimethylammonium bromide (CTAB, ≥98.0%) and sodium oleate (NaOL, ≥97.0%) were purchased from TCI Deutschland GmbH. HCl (37 wt% in water) was purchased from Carl Roth. n-heptane (95%) was purchased from Alfa Aesar. Liquid CO₂ was purchased from Westfalen. All chemicals were used as received without further purification.

**Nanostructure Synthesis:** TiO₂ Synthesis: TiO₂ nanoparticle synthesis was adopted from a previously published protocol.[32] While stirring, 1 mL of TiCl₄ was dropwise added to a 50 mL round bottom flask containing 5 mL of EtOH resulting in a transparent yellow solution. Next, 20 mL of benzyl alcohol were added and the solution was continuously stirred and heated to 80 °C while keeping the flask open. After 24 h the flask was immersed into a water bath at room temperature to quench the reaction. Next, the suspension was washed with diethyl ether (≈4.7 mL per mL suspension) by three dispersion-centrifugation cycles (3500 rpm, 5 min, room temperature). Afterwards, the supernatant was removed by decantation and the vial was loosely covered with its cap for 4.7 mL per mL suspension) by three dispersion-centrifugation cycles (3500 rpm, 5 min, room temperature). Afterwards, the supernatant was removed by decantation and the vial was loosely covered with its cap for slow evaporation of the remaining solvent. Finally, the dried precipitate was mortared to yield ≈550 mg of a white powder. TiO₂ nanoparticle characterization by DLS, X-Ray diffraction, and IR spectroscopy is shown in Figures S10 and S11, Supporting Information.

AuNP Synthesis: AuNP synthesis was adopted from a previously published protocol.[33] For this 37 mg sodium citrate tribasic dihydrate was added to a 250 mL round bottom flask containing 150 mL of water. Next, the flask was immersed into an oil bath which temperature was set to 120 °C. As soon as the solution started boiling, 375 mL of a 0.1 m HAuCl₄ solution was added and the solution turned from colorless to purple and red within a couple of minutes. After refluxing for 24 h at 120 °C, the dispersion was cooled down to room temperature and stored in a fridge for further use. AuNP characterization by TEM and UV/Vis absorbance spectroscopy is shown in Figure S12a–c, Supporting Information.

AuNR Synthesis: AuNR synthesis was adopted from a previously published seeded growth protocol.[30] The seed solution was prepared as follows: 5 mL of 0.5 mm HAuCl₄ was mixed with 5 mL of 0.2 m CTAB in a 30 mL scintillation vial. Next, 0.6 mL of fresh 0.01 m NaBH₄ was diluted to 1 mL with water and then injected into the HAUcCl₂-CTAB solution under vigorous stirring (≥1200 rpm). The stirring was stopped after 2 min. The yellow-brownish seed solution was aged at room temperature for 7–8 h before use.

To prepare the growth solution, 7.0 g of CTAB and 1.234 g of NaOL were dissolved in 250 mL of water in a 1 L Erlemeyer flask heated to 50 °C in a water bath. Next, the solution was cooled down to 30 °C and 18 mL of 4 mm AgNO₃ solution was added. The mixture remained undisturbed at 30 °C for 15 min, after which 250 mL of 1 mm HAuCl₄ solution was added. The solution became colorless after 90 min of stirring at 700 rpm and, after that, 2.1 mL of HCl was added. After another 15 min of slow stirring at 400 rpm, 1.25 mL of 64 mm ascorbic acid was added and the solution was vigorously stirred at ≥1200 rpm for 30 s.

Finally, 0.8 mL of seed solution was injected into the growth solution under vigorous stirring (1200 to 1500 rpm). The resultant mixture was stirred for 30 s and the stirring was turned off. The solution remained undisturbed at 30 °C for at least 12 h for the AuNR growth. The final product was isolated by centrifugation at 7000 rpm for 30 min followed by removal of the supernatant. Subsequently, AuNRs were redispersed in 10 mL of water. AuNR characterization by TEM and UV/Vis absorbance spectroscopy is shown in Figure S12d–f, Supporting Information.

**Ink Formulation:** Inks for 3D printing were formulated by dispersing a dry TiO₂ powder in a water/acetonitrile mixture (2:1 vol. ratio) yielding a mass loading of 15 wt%, which corresponds to a volumetric concentration of 4.0 vol%. The use of dry TiO₂ powder was necessary for reliably ink formulation with similar particle concentrations and rheological properties across multiple particle batches. The dispersing procedure consisted of a repetitive cycle of stepwise addition of TiO₂ nanoparticles, 1 min vortex mixing, followed by 1 min ultrasonication in an ice bath. An ice bath was used to impede temperature induced gelation due to frictional heating during vortex mixing. Multimaterial inks were formulated by replacing the corresponding volume fraction of water with an aqueous dispersion of AuNPs or AuNRs. For pH tests the neat TiO₂ ink was charged with 0.05 wt% methyl orange. Eventually, inks were stored in a refrigerator prior gelation. Before gelation, inks were homogenized two times for 5 min at 2000 rpm with a single degassing step of 5 min at 2500 rpm in between using an ARE-250 planetary speed mixer (Thinky Corporation, Japan). Gelation was performed in 5 cm² syringes in a preheated oven (60 °C) for 16.5 min while the open tip of the syringe was pointing upward. After gelation, the tip of the syringe was sealed with an airtight cap and the ink was typically used within 2 days.

3D Printing: Prints were performed in a liquid bath with an Engine HR 3D printer (Hyrel 3D, USA) equipped with multiple SDS-5 syringe displacement printheads. Syringes charged with the nanoparticle gel were loaded into the print head and equipped with Luer-Lock needles to define the filament diameter (150–1540 μm). Throughout this study either burr-free polished passivated stainless-steel nozzles from Nordson EFD or conical polyethylene nozzles from Gonano Dosiertechnik GmbH were used. For the former nozzle type the printed filaments appear smooth, whereas for the latter the surface was more uneven, as indicated in Figure 4b and 5c, respectively. Depending on needle diameter, prime and unprime values of the printhead were adjusted to achieve reliable start and stop of ink flow without oozing. Volumetric flowrate was calculated by the 3D printer’s software depending on needle diameter d, layer height (0.9 d), and printing speed (typical 2–6 mm s⁻¹). Before each print the distance of the nozzle and printbed was calibrated via an optical microscope camera (Dino-lite, USA). Printing paths were generated via custom-made Python-scripts.

The print itself was performed on silicon substrates coated with a PVP/PMMA bilayer. For this, silicon substrates (2.5 × 2.5 cm) were cleaned with acetone, isopropanol, and Milli-Q water in an ultrasonic bath and treated with air plasma for 5 min at 100 W (Femto, Diener Elektronik, Germany). For polymer deposition, the substrates were placed onto a spin-coater and fully covered with the polymer solution (First layer: 5 wt% PVP in EtOH. Second layer: 20 wt% PMMA in acetone) before starting the spinning process (PVP: 5 s at 500 RPM followed by 60 s at 1000 RPM, PMMA: 30 s at 3000 RPM). After each deposition cycle substrates were baked on a hotplate for 2 min at 50 °C.

Before the print, parts of the polymer bilayer along the edge of the substrate were removed to make the PVP layer more accessible for the lift off process after the print. As prepared substrate was fixed with 2 screws in a custom-made printing container that contained a liquid bath (Figure S4a,b, Supporting Information). The bath was obtained by vigorously shaking a mixture of 10 mL of n-heptane and 4 mL of an aqueous NH₃ solution in a flask. Next, the NH₃-enriched heptane phase was transferred to the printing container. During printing a fraction of the liquid bath was transferred back to the flask containing the NH₃ solution and the process of NH₃ enrichment was repeated every 5 min.

After the print, the liquid bath was refreshed a final time and the printing container was covered with a glass slide for 90 min. Subsequent, the substrate was immersed into a water/acetonitrile mixture (2:1 vol. ratio) for lift off (Figure S4c, Supporting Information). Finally, a stepwise solvent exchange to acetonitrile and CO₂ was supercritical drying in a Quorum E3100 was performed.

**Photothermal Measurements:** Aerogels were placed on a Teflon plate and illuminated with a 300 W Xe lamp equipped with a H₂O filter to remove IR light from the light source. For each measurement the distance of sample and light source was kept constant at 30 cm to illuminate all samples with similar light intensities. Temperature evolution was recorded with a high-resolution IR camera (SC7000, FLIR, USA). Transmission electron microscopy images were taken with a Regulus 8220 (Hitachi High Technologies Corp., Japan). The specific surface area and pore size were determined via the Brunauer–Emmet–Teller (BET) method and density functional theory (DFT) analysis, respectively. For DFT analysis a Non Local DFT
The data were corrected by a series of dark- and flat-field images and performed on MCR 502 rheometer (Anton Paar, Germany) in cone plate geometry (20 mm, 1°) with an attenuated total reflection module. Rheologic measurements were performed on a Bruker Alpha II spectrometer equipped with an attenuated total reflection module. Fourier transform infrared spectra were recorded using a Bruker Alpha II spectrometer equipped with an attenuated total reflection module. UV–vis-NIR absorbance spectra of nanoparticle dispersions and aerogel plates were recorded using an Agilent Cary 5000 spectrophotometer. A HeNe laser operating at 632.8 nm in backscatter detection mode. X-ray microtomography imaging was performed on a ZetaTas Nano ZS instrument (Malvern Instrument Ltd., UK) equipped with a HeNe laser operating at 632.8 nm in backscatter detection mode. X-ray microtomography imaging was performed on a custom-built setup as described elsewhere.[12] The X-ray microtube was operated at 60 kV and 50 µA. The sample was placed 111.2 mm from the source and 42.4 mm from the detector. For each scan 1440 projections were collected over 360° with an exposure time of 10 s. Projections were acquired at a magnification of 1.38 with an Andor Zyla sCMOS camera (2560 × 2560 pixels, 6.5 µm pixel size, 4x binning), resulting in an effective pixel size of 4 - 6.5 µm /4 = 1.38 µm. The data were corrected by a series of dark- and flat-field images and tomographically reconstructed in cone-beam geometry using a custom-made Python-script based on the ASTRA toolbox.[12] Reconstructed data were visualized and analyzed in Avizo software version 2020.2.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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3D printing, aerogels, hierarchical structures, metal oxides, nanoparticles, photothermal, plasmonics

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