Hierarchically Porous Ceramics via Direct Writing of Binary Colloidal Gel Foams

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ABSTRACT: Hierarchically porous ceramics with a high specific surface area and interconnected porosity may find potential application as particulate filters, catalyst supports, and battery electrodes. We report the design and programmable assembly of cellular ceramic architectures with controlled pore size, volume, and interconnectivity across multiple length scales via direct foam writing. Specifically, binary colloidal gel foams are created that contain entrained bubbles stabilized by the irreversible adsorption of attractive alumina and carbon (porogen) particles at their air–water interfaces. Composition effects on foam ink rheology and printing behavior are investigated. Sintered ceramic foams exhibited specific permeabilities that increased from $2 \times 10^{-13}$ to $1 \times 10^{-12} \text{m}^2$ and compressive strengths that decreased from 40 to 1 MPa, respectively, with increasing specific interfacial area. Using direct foam writing, 3D ceramic lattices composed of open-cell foam struts were fabricated with tailored mechanical properties and interconnected porosity across multiple length scales.

KEYWORDS: 3D printing, particle-stabilized foams, cellular ceramics, hierarchical porosity, particle filtration

1. INTRODUCTION

Hierarchical cellular structures are ubiquitous in nature due to their mechanical efficiency and multifunctionality.1−7 Inspired by natural systems, synthetic materials have been produced by bulk casting8−10 and additive manufacturing11−13 methods. Specifically, open- and closed-cell foams have been fabricated by casting particulate suspensions that contain pore-forming agents (porogens)8,14 as well as particle-stabilized foams.9,10,15 While ceramic foams can be readily generated, they are limited to simple 3D shapes that possess a bending-dominated mechanical response.13,16 Emerging efforts have focused on fabricating multiscale metamaterials via light-based 3D printing of photopolymerizable organic11,12,17−20 and preceramic resins.21 To date, 3D microlattices, octet trusses, and tetrakaidecahedra with struts composed of hollow shells,11,12,17,19 solid features,20,21 or even finer trusses17,18 have been produced that exhibit bending, stretching, or mixed-mode mechanical responses.

We recently introduced a new method for fabricating closed-cell ceramic foams and 3D periodic lattices, known as direct foam writing.13,16 Colloidal gel foam inks were developed that contained entrained bubbles stabilized by attractive colloidal particles, which irreversibly adsorb onto their liquid–air interfaces. These attractive colloidal particles also form a spanning network (or gel) in suspension. The printed 3D ceramic lattices exhibited high specific stiffness values that were superior to bulk foams and microlattices of similar total porosity produced via light-based 3D printing. However, their closed-cell struts lacked interconnected porosity needed for many applications of interest, including particle filtration,22 catalyst supports,23 and battery electrodes.24−26

To promote efficient fluid transport, one must create porous materials with tailored pore volume, size, and interconnectivity. Under high-velocity conditions, the pressure drop ($\Delta P$) across a given porous material is well described by eq 1, which combines Darcy’s law with Forchheimer’s extension

$$\frac{\Delta P}{L} = \frac{\eta v}{k} + \beta \rho v^2$$

where $L$ is the sample thickness, $v$ is the fluid velocity, $\eta$ is the dynamic viscosity of the fluid, $\rho$ is the fluid density, $k$ is the specific permeability, and $\beta$ is the inertial resistance. When the fluid velocity is low, eq 1 reduces to Darcy’s law. The characteristic pore diameter ($D$) and total porosity, defined by the pore fraction ($\epsilon$), control the specific permeability ($k$)

$$k = \frac{\epsilon^3}{150(1-\epsilon^2)} D^2$$

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As a benchmark, the reported permeability of porous ceramics used in wall-flow diesel particulate filters, where $D_{\text{wall}} \sim 10 \mu m$ and $\epsilon_{\text{wall}} \sim 0.4$–0.5, ranges between $k \sim 10^{-13}$ and $10^{-12}$ m$^2$.\textsuperscript{27}

Here, we report the design and programmable assembly of hierarchically porous ceramics via direct writing of binary colloidal gel foams. We created foam-based inks composed of a mixture of hydrophobically modified alumina and carbon (porogen) particles that irreversibly adsorb onto liquid—air (bubble) interfaces\textsuperscript{8,13,15,28,29}. We then investigated the foam ink rheology and printing behavior. Next, we produced hierarchically porous ceramics by both bulk casting and direct foam writing. Upon sintering, the resulting hierarchically porous ceramics contain open walls (macropores), arising from the removal of porogen particles, that surround open cells (mesoscale pores) generated by entrained bubbles. Unlike the cast structures, the printed and sintered 3D ceramic lattices contained a third level of hierarchy resulting from the interconnected pathways (macropores) between patterned features. Finally, we assessed their microstructural evolution, permeability, and compressive mechanical properties to elucidate the effects of hierarchical porosity on their performance.

2. EXPERIMENTAL SECTION

2.1. Binary Colloidal Gel Foams. Binary colloidal gels and foam-based inks are produced by first dispersing an appropriate amount of α-alumina particles (AKP 30 Sumitomo Chemical) with a mean particle size, $D$, of 300 nm and a specific surface area of $\sim 7.5$ m$^2$/g in deionized (DI) water at a pH $> 10$ (adjusted by adding sodium hydroxide, NaOH). The resulting alumina (stock) suspension is ball milled for 1 week using alumina milling media. Next, carbon black (porogen) particles (Thermox N990, Cancarb LTD; $d_{50} = 280$ nm and Brunauer–Emmett–Teller surface area $\sim 9.4$ m$^2$/g) are added in a step-wise fashion to the stock suspension. The suspension is then mixed for 2 min at 2200 rpm in a planetary mixer (SpeedMixer DAC 600.2; FlackTek, Inc.) after each step-wise carbon black addition. The resulting alumina/porogen particle ratio is 30:70 by volume, which ensures a high degree of porosity without compromising mechanical robustness. Next, an amine surfactant (decmamine, 95%; Sigma-Aldrich) is added to partially hydrophobize both particle populations. The specific concentration ($c$) is varied between 0.3 and 1.2 mmol of decamlylene per m$^2$ of total particle surface area. The surface tension of each corresponding supernatant solution is measured using the pendant-drop method (Kruss DSA100 Goniometer). The drop geometry is imaged at a rate of 10 frames/s, while its volume is increased at a rate of 10 μL/min.\textsuperscript{15} To prevent cracking during drying of the cast and 3D printed foams, we incorporated 1 wt % of poly(ethylene glycol) (PEG, $M_w \sim 20,000$; Sigma-Aldrich) and 1 wt % sucrose as binders. Each suspension is diluted to a total colloidal volume fraction between 0.11 $< \phi < 0.18$ prior to homogenization in a planetary mixer.

Binary colloidal gels are created by adjusting the pH to a value of 10.25 to induce attractive interactions between both particle populations. These precursor gels are transformed into the desired foam-based inks by mechanical frothing using a four-bladed impeller (316L Cross Stirrer; Scilogex) attached to an overhead mixer (4-bladed vane (15 mm diameter, 38.5 mm height, 1.3 mm blade thickness, 4 mm gap) and a solvent trap to prevent evaporation. The foams are loaded into the cup immediately after frothing. Prior to the measurements, foams are equilibrated under a low-amplitude oscillatory strain ($\gamma = 0.001$) until $G'$ remains approximately constant (typically 15–30 min). After equilibration, stress sweeps are carried out between 0.01 and 250 s$^{-1}$. Their shear yield stress ($\tau_y$) is defined by the crossover point, where $G'$ exceeds $G''$.

2.3. Foam Casting and Printing. Bulk foams are created by casting foam-based inks into rectangular plastic molds ($60 \times 25 \times 10$ mm), which are precoated with a thin layer of petroleum jelly to facilitate removal. During the casting process, each mold is manually shaken to ensure proper filling and any excess foam is removed using a doctor blade to produce bulk foams with flat (top) surfaces. 3D ceramic lattices are produced by the direct writing of foam-based inks. Specifically, each foam ink is loaded into a 60 mL syringe and dispersed through a tapered nozzle (Nordson EFD) with varying inner diameter using a syringe pump (PHD Ultra; Harvard Apparatus). Most 3D lattices are printed using a nozzle with a 610 μm inner diameter. The printhead is attached to a custom-built 3D printer (ABG 10000; Aerotech Inc.), whose $x$–$y$–$z$ motion is controlled by a customized G-code. Square lattice structures are printed at 37 mm/s with a flow rate of 2.1 mL/min into 18 $\times$ 18 $\times$ 12 mm shapes utilizing wax-coated (Pure Petroleum Jelly; Vaseline) zirconia plates (Zircoa) as substrates for the ink deposition.

Both cast and printed foam structures are slowly dried under controlled humidity conditions for several days. After drying at room temperature, they are removed from the substrates and heated at 90 °C for 4 h to remove any residual water from the samples. The samples are then heated to 700 °C at 2 °C/min for 3 h to remove the carbon (porogen) particles, followed by heating to 1500 °C at 2 °C/min, where they are held for 2 h, to sinter the alumina particles prior to cooling to ambient temperature.

2.4. Microstructural Evolution. The microstructural evolution of cast and printed foams is characterized using field-emission scanning electron microscopy (Ultra55 Zeiss) after both drying and sintering. Image analysis is carried out to determine the average bubble diameter ($d$) and average bubble volume fraction ($\phi$) for each foam sample. Note that the bubbles represent the dispersed phase, while the alumina/porogen particle matrix (or, after sintering, pure alumina) serves as the continuous phase within these foams. The specific bubble surface area ($\Sigma$, m$^2$/mm$^3$ or mm$^3$), which is reported per unit volume of foam, is calculated by $\Sigma = (b\phi/d) \times 1000$, where $\phi_b$ and $d$ (μm) are measured experimentally.\textsuperscript{16} $d$ is obtained using the linear intercept method for two-phase materials (ASTM E112-13), in which at least 40 mm of lines are analyzed over 5 mm$^2$. $\phi_b$ is obtained using the systematic point count method (ASTM E562-08),\textsuperscript{16} in which at least 400 grid points are analyzed over 5 mm$^2$ for each dried foam sample. The reported averages and standard deviations correspond to values obtained from at least three different images.

2.5. Porosity, Permeability, and Particle Filtration Measurements. The porosity of sintered ceramic foams is characterized using mercury intrusion porosimetry (Micromeritcs AutoPore). Prior to testing, the samples are heated to 350 °C for 1 h and then cooled to room temperature. The samples are analyzed using a fixed pressure table, which ranges from 1.5 to 60,000 psi, with a 10 s equilibration at each pressure. A blank is run and subtracted from the data. The data are analyzed using the Washburn equation, $D = (4\gamma \cos \psi)/P$, where $\gamma$ is the surface tension of mercury ($\gamma = 0.48$ N/m), $q$ is the advancing and receding contact angle ($\psi = 140^\circ$), $D$ is the pore diameter, and $P$ is the pressure. The relative density ($\rho_{rel}$) of each sample is calculated based on the total volume of mercury intruded, where $\rho_{rel} = \rho_o/\rho_o \times 100$% and $\rho_o$ is the theoretical density of alumina ($\rho_o = 3.97$ g/cm$^3$).

The permeability, $k$, of the sintered ceramic foams is measured by flowing air at a rate $(Q)$ of 0.5–1 L/min through disc-shaped samples (thickness, $L$, of ~1 mm) and a cross-sectional area ($A$) of ~960 mm$^2$ and measuring the pressure drop ($\Delta P = p_h - p_l$) using

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pressure transducers. $k$ is given by Darcy’s law, $Q = \frac{kA (p_b - p_a)}{L} = -\mu \frac{dA}{dx}$, where $\mu$ is the dynamic viscosity of air, and $p_b$ and $p_a$ are the gas pressure measured on each side of the foam disc.

To assess their particle filtration capability, we first prepared an aqueous suspension by mixing 1 $\mu$m-sized fluorescent polystyrene beads (PS, FluoSpheres Carboxylate-Modified Microspheres, 1.0 $\mu$m, crimson fluorescent (625/645), 2 wt % solids; Thermo Fisher Scientific) with DI water to yield a dilute PS suspension (3 $\times$ 10$^{-4}$ wt % solids). We then flowed 500 ml of this dilute PS suspension through a sintered Al$_2$O$_3$ foam (14% of theoretical density) cast in the form of a disc (20 mm in diameter, 3 mm in thickness). After filtration, the foam discs are imaged using a laser scanning confocal microscope (Zeiss LSM 710) to determine the location of the fluorescent PS particles.

2.6. Mechanical Property Measurements. Sintered (cast and printed) foams prepared at different mixing intensities and, hence, relative densities are tested under compression (Instron 5566) at a displacement rate of 1 $\mu$m/s. The top and bottom surfaces of each specimen are polished to ensure a uniform load distribution. The yield strength ($\sigma_y$) is defined by the stress at which 0.2% plastic deformation occurs, while the elastic modulus ($E$) is defined by the slope of the stress versus strain curve between 50 and 80% $\sigma_y$.

3. RESULTS

3.1. Binary Colloidal Gel Foams. A two-step process is used to create foam-based inks for the direct writing of hierarchically porous ceramics. In the first step, a binary colloidal gel is produced by mixing 1 $\mu$m-sized fluorescent polystyrene beads (PS, FluoSpheres Carboxylate-Modified Microspheres, 1.0 $\mu$m, crimson fluorescent (625/645), 2 wt % solids; Thermo Fisher Scientific) with DI water to yield a dilute PS suspension (3 $\times$ 10$^{-4}$ wt % solids). We then flowed 500 ml of this dilute PS suspension through a sintered Al$_2$O$_3$ foam (14% of theoretical density) cast in the form of a disc (20 mm in diameter, 3 mm in thickness). After filtration, the foam discs are imaged using a laser scanning confocal microscope (Zeiss LSM 710) to determine the location of the fluorescent PS particles.

Figure 1. Binary colloidal gel foams. (a) In aqueous-based binary gels, both alumina and carbon (porogen) particles are similarly hydrophobized with amphiphilic surfactant molecules in a single step. (b) After the incorporation of air by mechanical frothing, both types of particles are driven to the bubble/water interfaces. In the inset, the irreversible adsorption of the particles to the interfaces is quantified by a contact angle of around 90°, with partial wetting from both fluid phases. (c) Schematic view of direct writing of binary colloidal gel foams into filaments. (d) Zeta potential vs pH plot for both particle populations. (e,f) Plots of apparent viscosity as a function of shear rate and storage ($G'$) and loss moduli ($G''$) as a function of shear stress ($\tau$) for a representative binary colloidal gel before and after mechanically mixing to create a foam ink.

$$\Delta E = \pi r_p^2 \gamma_{lg} (1 - \cos \theta)^2, \quad \theta < 90^\circ$$

where $r_p$ is the particle radius, $\gamma_{lg}$ is the liquid–air interfacial energy, and $\theta$ is the contact angle (Figure 1b). Since both particle populations have similar radii, their $\Delta E$ values should be comparable based on eq 3. The measured values of $\gamma_{lg}$ range from 72.8 mN/m, the value for pure water, to $\sim$60 mN/m over the range of surfactant concentrations probed (Figure S1). When $\theta = 14°$–90°, the calculated particle attachment energy exceeds $10^3 k_B T$, where $k_B$ is the Boltzmann constant and $T$ is the absolute temperature for both particle populations. Stabilization of the liquid–air interface prevents bubbles entrained within binary colloidal gels from coalescing due to van der Waals forces or Ostwald ripening. In fact, the resulting binary colloidal gel foams exhibit a stable foam microstructure in
the wet state that remains unchanged during storage over periods ranging from several days to weeks. These foam-based inks enable the fabrication of hierarchically porous ceramic architectures via direct foam writing (Figure 1c). To drive the surfactant adsorption, the inks are adjusted to a pH > 10 to induce a negative charge on both alumina and carbon particles (Figure 1d). Despite their relatively high zeta potential values (−25 mV for alumina and −45 mV for carbon) under these conditions, these hydrophobically modified particles undergo gelation leading to the desired viscoelastic response for direct ink writing. For example, the binary colloidal gel and foam inks (Λ = 0.9 μmol/m², pH = 10.25, Φf = 0.14) exhibit a strong shear-thinning behavior (Figure 1e), with apparent viscosity values ranging from ~4 × 10⁴ Pa·s at 10⁻³ s⁻¹ to ~0.07 Pa·s at 10³ s⁻¹ (gel inks) and from ~6 × 10⁴ Pa·s at 10⁻³ s⁻¹ to ~0.11 Pa·s at 10² s⁻¹ (foam inks). Moreover, these inks also exhibit a solid-like response; that is, their storage modulus (G’) exceeds their loss modulus (G″), in the linear elastic regime, with G’ values of ~3 × 10⁴ Pa (gels) and ~10⁵ Pa (foams) at their corresponding shear yield stresses of τᵧ ≈ 25 Pa and τᵧ ≈ 100 Pa. Unless otherwise stated, the binary colloidal gels used to create foam inks in the present work are produced using the following standard conditions: Λ = 0.9 μmol/m², pH = 10.25, and Φf = 0.14.

Controlling the foam ink microstructure is crucial to achieving hierarchically porous ceramics with open cells (mesoscale pores) surrounded by microporous cell walls. The bubble volume fraction and characteristic size are greatly influenced by the foaming intensity used during mechanical frothing (Figure 2) as well as the surfactant concentration (Figure S2). To explore the effects of mixing intensity, we created a standard binary colloidal gel with a constant alumina to carbon volume ratio of 30:70. As the foaming intensity increased from 50 to 100%, we observed pronounced microstructural changes (Figure 2a−d). Indeed, we find that the average bubble size, d, decreases from ~135 to ~40 μm, while the bubble volume fraction, Φff, increases from ~0.6 to ~0.8 (Figure 2e) over these frothing conditions. During this process, the binary colloidal gel network is subjected to high shear rates that disrupt the attractive bonds between particles allowing them to adsorb onto the liquid–air interface during air entrainment. The specific interfacial area Σ increases from ~30 to ~120 mm²/mm³ as Φf increases (Figure 2f), driving even more particles to the bubble walls. Once mechanical frothing ceases, the attractive particle network quickly reforms around each entrained bubble resulting in stiffer foam inks, where G’ increases from ~3 × 10⁵ Pa (gel) to ~4 × 10⁶ Pa (foam, 50% mixing intensity) to ~8 × 10⁶ Pa (foam, 100% mixing intensity) (Figure 2g). Since the adsorption energy of particles at the liquid–air interface is at least 2 orders of magnitude higher than the estimated attractive interactions between particles within the (bulk) gel network (e.g., ≥10⁵ k_BT vs ~10⁹ k_BT), we posit that the enhanced foam ink elasticity arises from a greater connectivity between interspersed bubbles within the gel matrix. Importantly, we find that ink stiffness increases linearly with Σ (Figure S3) akin to unary colloidal foam inks reported previously.16

The foam ink microstructure and stiffness also depend on the composition of the binary colloidal gels mechanically frothed at a constant mixing intensity (Figure S2a−d). As one example, we changed the particle hydrophobicity by varying the surfactant concentration. For foam inks generated at 100% mixing intensity, the average bubble size decreases from ~100 to ~40 μm, as Λ increases from 0.3 to 0.9 μmol/m² (Figure S2e). However, no further reduction in characteristic bubble size is observed at higher surfactant concentrations, that is, Λ = 1.2 μmol/m², suggesting that the particle surfaces are already saturated. Over this same surfactant concentration range, Φf increases from ~0.67 to ~0.84 (Figure S2e), resulting in a concomitant increase in Σ from ~35 to ~120 mm²/mm³ (Figure S2f). These microstructural changes result in an increased foam ink stiffness that ranges from G’ ~ 2 × 10⁵ at Λ = 0.3 μmol/m² to G’ ~ 10⁶ Pa at Λ = 1.2 μmol/m² (Figure S2g).

Figure 2. Mixing effects on binary colloidal gel foam microstructure and elasticity. (a−d) Micrographs of dried green foams obtained with 50, 70, 85, and 100% mixing intensity protocols, respectively. Plots for (e) average bubble size, d, bubble volume fraction, Φf, and (f) specific interfacial area, Σ, vs mixing intensity. (g) Storage moduli [G’] as a function of shear stress [τ] for foams subjected to the different mixing protocols.
Intensities corresponding to relative densities, $\rho$ (lowest three representative sintered ceramic foams prepared at 50% carried out mercury intrusion porosimetry measurements on micropores within the open-cell walls range in size from bubbles, range in diameter from that the mesoscale pores, associated with entrained air $\sim$ cast and dried) to $\sim$ ceramic foams (produced at 100% mixing intensity) undergo reduction in their average bubble size from $\sim$ microporous cell walls are achieved with a characteristic thickness of $\sim$ 1 $\mu$m. These representative ceramic foams (produced at 100% mixing intensity) undergo $\sim$ 23% linear shrinkage during sintering, leading to a reduction in their average bubble size from $\sim$40 $\mu$m (as-cast and dried) to $\sim$31 $\mu$m (sintered) (Figure 3a), as summarized in Table 1. Microporous cell walls are achieved using an alumina/carbon particle ratio of 30:70 by volume (Figures S4 and 3b). To further assess their porosity, we carried out mercury intrusion porosimetry measurements on three representative sintered ceramic foams prepared at 50% (lowest $\Sigma$), 85% (medium $\Sigma$), and 100% (high $\Sigma$) mixing intensities corresponding to relative densities, $\rho_{\text{rel}}$ of $\sim$24, $\sim$14, and $\sim$10%, respectively (Figure 3c). These data reveal that the mesoscale pores, associated with entrained air bubbles, range in diameter from $\sim$10 to 150 $\mu$m, while micropores within the open-cell walls range in size from $\sim$0.3 to $\sim$4 $\mu$m in diameter (Figure 3d). These fine pores arise when either individual carbon (porogen) particles or clusters volatilize when heated in an oxidative environment during the sintering process.

Table 1. Properties of Binary Colloidal Gel Foams

<table>
<thead>
<tr>
<th>Foam type</th>
<th>Binary colloid gel foams (cast and dried)</th>
<th>Hierarchically porous foams (sintered)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bubble size ($\mu$m)</td>
<td>Bubble volume (%)</td>
</tr>
<tr>
<td>Lowest $\Sigma$</td>
<td>135</td>
<td>61–62</td>
</tr>
<tr>
<td>Low $\Sigma$</td>
<td>84</td>
<td>74</td>
</tr>
<tr>
<td>Medium $\Sigma$</td>
<td>47</td>
<td>77</td>
</tr>
<tr>
<td>High $\Sigma$</td>
<td>41</td>
<td>82</td>
</tr>
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3.2. Microstructural Evolution and Properties of Hierarchically Porous Ceramic Foams. Sintered ceramic foams possess an open, hierarchically porous microstructure (Figure 3). Scanning electron microscopy (SEM) images reveal large pores (10’s $\mu$m in diameter) corresponding to entrained bubbles, which are surrounded by fine porous walls with a characteristic thickness of $\sim$1 $\mu$m. These representative ceramic foams (produced at 100% mixing intensity) undergo $\sim$23% linear shrinkage during sintering, leading to a reduction in their average bubble size from $\sim$40 $\mu$m (as-cast and dried) to $\sim$31 $\mu$m (sintered) (Figure 3a), as summarized in Table 1. Microporous cell walls are achieved using an alumina/carbon particle ratio of 30:70 by volume (Figures S4 and 3b). To further assess their porosity, we carried out mercury intrusion porosimetry measurements on three representative sintered ceramic foams prepared at 50% (lowest $\Sigma$), 85% (medium $\Sigma$), and 100% (high $\Sigma$) mixing intensities corresponding to relative densities, $\rho_{\text{rel}}$ of $\sim$24, $\sim$14, and $\sim$10%, respectively (Figure 3c). These data reveal that the mesoscale pores, associated with entrained air bubbles, range in diameter from $\sim$10 to 150 $\mu$m, while micropores within the open-cell walls range in size from $\sim$0.3 to $\sim$4 $\mu$m in diameter (Figure 3d). These fine pores arise when either individual carbon (porogen) particles or clusters volatilize when heated in an oxidative environment during the sintering process.

Next, we explored the effects of hierarchical foam porosity on their fluid transport and filtration properties. Representative sintered ceramic foams with relative densities of $\rho_{\text{rel}}$ $\sim$ 10% (high $\Sigma$), $\rho_{\text{rel}}$ $\sim$ 14% (medium $\Sigma$), and $\rho_{\text{rel}}$ $\sim$ 19% (low $\Sigma$) are prepared from standard binary colloidal gels mechanically frothed at different mixing intensities. We measured the normalized pressure drop $\Delta P/L$ across each foam sample as a function of gas velocity (Figure 4a) and used eq 2 to calculate their permeability (Figure 4b). Their estimated $k$ values lie within a relatively narrow range, decreasing from $9 \times 10^{-13}$ to $2 \times 10^{-13}$ m$^2$ with increasing relative density. This observation likely reflects tortuosity effects that arise as the thickness of bubble walls increases. Since their measured permeability is akin to values reported for commercial diesel particulate filters, we explored their ability to filter fluorescent PS particles representative of diesel exhaust ($\sim$1 $\mu$m in diameter) (Figure 4c). Confocal microscopy reveals that a thin, relatively dense layer of PS particles accumulates onto the foam surface. The corresponding cross-sectional images of these foams shows that $>99\%$ of the PS particles are trapped within the first 100 $\mu$m of these structures. We note that their filtration efficiency may be further enhanced due to electrostatic attractions between the oppositely charged particles and the ceramic foam.

To determine their mechanical properties, we carried out compression tests on several sintered ceramic foams with
We posit that this discrepancy arises due to the hierarchically porous nature of our ceramic foams, which consist of discrete mesoscale bubbles surrounded by microporous cell walls. By contrast, conventional (reticulated) ceramic foams contain mesoscale pores that are interconnected via open windows between adjacent cells and surrounded by dense slender beams. Further study of this new class of hierarchical ceramic foams is needed to fully understand their observed scaling behavior.

3.3. Direct Writing of 3D Ceramic Foam Lattices. To introduce controlled porosity at the macroscale, we printed foam-based inks through a fine nozzle (610 μm in diameter) at a speed of 37 mm/s to produce 3D ceramic foam lattices (Figure 6a–d). The printed lattices consist of a simple cubic (or tetragonal) geometry with 20 printed layers, overall dimensions of 18 mm × 18 mm × 12 mm and a center-to-center spacing of ∼2 mm between adjacent struts. During sintering, they exhibit an isotropic, linear shrinkage of ∼23% and retain their hierarchical open-cell morphology. Akin to their bulk (cast) counterparts, the 3D lattice struts contain mesoscale pores that arise from entrained bubbles surrounded by microporous cell walls that are generated upon the removal of carbon black porogen particles during sintering. Additionally, these 3D lattices contain an 8 × 8 array of interconnected macroscale porous features that reside between printed struts. We established a printing window for direct writing of these binary colloidal gel foam inks by exploring a range of nozzle diameters (330–840 μm) and print speeds (5–200 mm/s), as shown in Figure 6e. While these foam-based inks exhibit clogging in the finest nozzles tested, they flow readily through larger nozzles. At the lowest print speed, the inks dried too quickly to ensure high fidelity printing, while printing at the highest speed led to slightly discontinuous features.

Last, we measured the yield strength of sintered ceramic foam lattices of varying total porosity and Σ values (Figure 6f) under compression along the z-axis, which is orthogonal to the printed struts that are orthogonally patterned in a layerwise manner in the x–y plane. Due to their hierarchical porosity across three length scales, these 3D ceramic lattices possess low relative densities ranging from roughly 3 to 6%  \( \rho_{th} \). Akin to the sintered (cast) ceramic foams described above, the yield strength of these printed ceramic foams exhibits a power law dependence on relative density, where  \( n \sim 2.5 \). We also find that these 3D foam lattices exhibit higher compressive strength values, for example,  \( \sigma_y \sim 2 \text{ MPa} \) at  \( \rho_{th} \sim 5.5\% \) compared to bulk (cast) foams, which must have twofold higher density ( \( \rho_{th} \sim 11\% \)) to achieve a comparable  \( \sigma_y \sim 2 \text{ MPa} \). Hence, by programming their open porosity across multiple length scales from the foam struts that contain mesoscale open cells surrounded by microporous walls to their 3D lattice geometry, we can tailor their permeability and mechanical properties for targeted applications of interest.

4. CONCLUSIONS

We have designed and assembled bulk and 3D printed ceramic foams with hierarchical open porosity tailored across multiple length scales. By creating binary colloidal gels that...
contain hydrophobically modified ceramic and porogen particles, we produced foam-based inks in which both particle populations adsorb at the liquid–air interfaces of entrained bubbles generated via mechanical frothing. We showed that the characteristic bubble size and volume fraction depended on both the binary colloidal gel composition and the mixing

Figure 5. Mechanical behavior of hierarchically porous ceramic foams. (a) SEM images of representative sintered ceramic foams with low, medium, and high Σ values. (b) Stress–strain plots for representative sintered ceramic foams with lowest , medium, and high Σ values. (c,d) Log–log plots of the Young’s modulus (E) and yield strength (σy) as a function of sintered ceramic foam density for representative samples of varying Σ values, both showing a power dependence with density depicted as a dotted line.

Figure 6. Direct foam writing of hierarchically porous ceramic architectures. (a) Optical image of representative printed and sintered hierarchical ceramic foam lattice. (b) SEM image of the cross-section of a printed and sintered hierarchical ceramic foam lattice showing large pore channels between printed foam struts. (c) Higher magnification SEM image of entrained bubbles within a strut in the printed and sintered hierarchical ceramic foam lattice. (d) Microstructure of a representative bubble wall. (e) Processing window for 3D printing of binary colloidal gel foams. [Note: black data points reside in the printing region]. (f) Log–log plot of yield strength as a function of sintered hierarchical ceramic foam density for printed and cast (bulk) foams of varying Σ values measured under compression along the z-axis (out-of-plane direction in Figure 6a).
intensity used during mechanical frothing. We further showed that the incorporation of carbon black porogen particles that are removed during sintering in an oxidative environment leads to open-cell walls that surround the entrained bubbles. Using direct foam writing, we printed 3D ceramic foam lattices that exhibit enhanced permeability and mechanical properties compared to bulk foams of similar relative density. Our integrated design and fabrication platform may open new avenues to creating programmable ceramic foams for myriad applications, including particle filtration, catalyst supports, and novel electrodes for flow batteries.

**REFERENCES**


