Printing spongy all-in-liquid materials

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Article

Keywords:

Posted Date: February 4th, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1009268/v2>

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Version of Record: A version of this preprint was published at Nature Communications on July 18th, 2022. See the published version at <https://doi.org/10.1038/s41467-022-31644-2>.

Printing spongy all-in-liquid materials

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1 Abstract

Printing structured networks of functionalized droplets in a liquid medium enables engineering collectives of living cells for functional purposes [1, 2], bacterial ecology [3], and promises enormous applications in processes ranging from energy storage [4, 5] to drug delivery [6, 7] and tissue engineering [8]. Current approaches are limited to drop-by-drop printing [1, 2] or face limitations in reproducing the sophisticated internal features of a structured material and its interactions with the surrounding media [6, 9–11]. Here, we report on a simple approach for creating stable liquid filaments of silica nanoparticle dispersions and use them as inks to print all-in-liquid materials that consist of a network of droplets. Silica nanoparticles stabilize liquid filaments at Weber numbers two orders of magnitude smaller than previously reported in

liquid-liquid systems by rapidly producing a concentrated microemulsion zone at the oil-water interface. We experimentally demonstrate that the printed aqueous phase is emulsified in-situ; consequently, a 3D structure is achieved with flexible walls consisting of layered microemulsions. The tube-like printed features have a spongy texture resembling miniaturized versions of “tube sponges” found in the oceans. A scaling analysis based on the interplay between hydrodynamics and emulsification kinetics reveals that liquid filaments are formed when emulsions are generated and remain at the interface during the printing period. We demonstrate the utilization of filaments of the nanoparticle dispersions for printing fluidic channels and propose to use them as lab-on-a-chip devices.

2 Introduction

Recently developed liquid-in-liquid printed materials [6,10–14] have many potential applications in energy storage [4,5], microreactors [7], and for creating biomimetic materials [8,15]. These types of materials are generated by the jamming of nanoparticles at the oil-water interface by application of an electrical field [16], using molding [11,17], or direct ink writing (DIW) printing techniques [10,12]. The materials lack the multiscale porosity created by emulsion-based inks used in 3D printed solid structures [18–20]. Emulsions allow encapsulating hydrophilic and hydrophobic cargoes together into the same printed texture [21,22]. Also, emulsions enable interactions between the printed frame and the surrounding media, where the space within the printed texture, i.e., porosity, is controlled by the droplet size distribution [18–20]. Although emulsions are ideal colloidal dispersions for printing in air, their utilization in liquid printing systems is limited to sticky (gel-like) emulsions [23]. The stability of the emulsion is the main

challenge that hinders their applications as inks in liquid media. Either the injected emulsion phase is immediately dispersed in the surrounding liquid, or the droplets swell and coalesce. Consequently, conventional emulsions are not appropriate candidates for printing in liquid media.

We describe a new approach to print porous liquids in a liquid medium. Silica nanoparticles are incorporated into spontaneous emulsification systems of sorbitan monooleate (Span 80) micellar solutions. Upon contacting an oleic micellar solution with the aqueous silica dispersion, nanoscale droplets nucleate inside the micellar solution close to the oil-water interface, forming a microemulsion phase. The rapid expansion of the interfacial area due to the low oil-water interfacial tension creates interconnected structures of oil and microemulsion phases. The spontaneous formation of a bicontinuous phase at the oil-water interface and its further penetration inside the bulk stabilizes liquid filaments with porous walls that can be used as inks for liquid-in-liquid printing.

3 Results and Discussion

3.1 Morphological states of liquid columns

The aqueous phase (de-ionized (DI) water or 4.0 wt.% silica dispersion) is injected with an average speed $8.0 \times 10^{-4} - 1.1 \times 10^{-1}$ m/s into a mineral oil reservoir containing 20.0 wt.% Span 80 micellar solutions. The oil viscosity is 135 mPa.s, while the addition of Span increases the oil viscosity to 257 mPa.s (**Fig. S1b**). For the case of DI water, single drops detach from the injection needle tip and sediment through the micellar solution, as is familiar from the

Plateau-Rayleigh instability (**Fig. 1a**). The injection of a 4.0 wt.% silica dispersion generates three flow regimes (**Fig. 1b**). These flow morphologies were characterized by a fast Fourier transform analysis (Supporting information, section III) and named bead-on-a-string (BOAS), column, and connected, and color coded respectively in blue, green, and red throughout the manuscript (**Fig. 1** and Supporting Movies 1-4).

The BOAS regime appears for the lowest injection speeds, where the detached drops merge with the preceding drops, and is identified with the dominant wavelength of $1.9 \text{ mm} < \lambda_{\text{mean}} < 2.6 \text{ mm}$. Please note that the column and connected flow regimes do not have a dominant wavelength (Supporting information, section III). Thus, we consider the cut-off wavelength, where the power spectrum starts reducing, as the characteristic wavelength in column and connected flow regimes. In the column state, which occurs for intermediate injection speeds, the injected liquid forms a stable thread-like shape without breaking into droplets, where the cut-off wavelength is $0.7 \text{ mm} < \lambda_{\text{cut-off}} < 1.0 \text{ mm}$. The connected regime occurs at high injection speeds, where a thread connects the neighbouring droplets, i.e., a combination of column and BOAS shapes, with wavelengths of $2.5 \text{ mm} < \lambda_{\text{cut-off}} < 3.2 \text{ mm}$ (**Fig. 1b,c**). Here, our particular interest is on identifying conditions that lead to the column regime since stable columns have potential applications for direct ink writing, as we demonstrate below.

Additional experiments are conducted over a range of silica concentrations 0.0, 1.0, 2.0, and 4.0 wt.% and Span concentrations 1.0, 5.0, 10.0, 20.0 and 40.0 wt.% (**Figs. S2-5**). Although many research papers report liquid filaments that are formed at Weber numbers ($We = \rho_i U^2 d_i / \gamma$, where ρ_i , d_i , U and γ are the density of the aqueous phase, inner diameter of the needle, injection speed, and interfacial tension) close to unity [9, 24–26], we report the

stabilization of liquid columns at $We \gtrsim O(0.001)$ (**Fig. 1d**), indicating that inertia is not the dominant force that overcomes the surface tension force in our experiments. Further experiments over a range of micellar solution viscosities from $\mu = 30$ to 1000 mPa.s (see **Figs. S14** and **S16**) reveal that liquid columns are formed in silica-Span systems with $\gamma_{eq} = O(0.01)$ mN/m and $\mu > 60$ mPa.s (Supporting information, section V).

Previous studies report two pathways for the formation of stable liquid columns in a liquid medium: i) jamming of nanoparticle and end-functionalized polymer entities at the oil-water interface [6, 10] and ii) a change of the micelle morphology from spherical to lamella at the oil-water interface [9, 27]. In the former, dispersed nanoparticles in the aqueous phase interact with end-functionalized polymers in the oil phase, forming surface-active nanoparticles that are locked at the interface and prevent or delay the Plateau-Rayleigh instability [6, 10]. In the latter, lamella structures are produced from the interfacial reaction of dissolved spherical cationic micelles in the aqueous phase and a fatty acid oil phase [9, 27]. However, we observe that liquid columns are only formed in Span micellar solutions above 10 wt.% (**Fig. 1** and **Figs. S2-5**). Thus, the surface-activation of silica nanoparticles is not the responsible mechanism for the formation of liquid columns as silica nanoparticles can be surface-activated at much lower Span concentrations (below 1.0 wt.%) [28, 29]. To investigate the possibility of the second mechanism, i.e., reconstruction of a micellar morphology in the presence of silica nanoparticles, we visualize the structure of the interfacial layer with and without silica particles as presented in the next section.

Figure 1: Flow regime morphologies of a (a) DI water and (b) 4.0 wt.% silica dispersion injected into a 20.0 wt.% Span micellar solution. The scale bar is 1 mm. (c) A plot of the wavelength versus the flow rates identifies four morphologies as single droplet (black), BOAS (blue), liquid column (green), and connected droplet (red), as characterized based on a Fast Fourier Transform (FFT) analysis (see supporting information, section II). (d) Flow regime map of tested Span and silica concentrations at various injection flow rates, where the latter is represented using the Weber number. The map indicates the formation of liquid columns at $We = O(0.01)$.

3.2 Effect of nanoparticles on the formation of liquid columns

A droplet (volume $V = 2 \mu\text{l}$) of the aqueous phase is placed in the bulk of a 20.0 wt.% Span micellar solution, close to a transparent solid surface (**Fig. S13a**). Images are recorded from the bottom of the container over 24 hours as shown in **Fig. 2a,b**. Initially, a dark zone is formed at the aqueous phase-oil interface, with an intensity that decreases over time on the DI water droplet (**Fig. 2a. 1 – 6**), while it remains constant on the silica droplet (**Fig. 2a. 1' – 6'**). Cryo-SEM images are taken after 24 hours from the water-Span micellar solution interface, as shown in **Fig. 2a**, panels 7 – 8, which reveal the spontaneous formation of a microemulsion zone in which submicrometer water droplets (light gray) are dispersed in the oil phase (dark gray). The water droplets are Span micelles that are filled with water after being in contact with the aqueous phase, hence forming the emulsion phase.

In the presence of silica nanoparticles (**Fig. 2a. 7'**), the droplets in the microemulsion phase are more concentrated as compared with the case without silica. However, the droplets in both systems (with and without silica) are spherical, indicating that the Span micelle structure remains unchanged in the presence of nanoparticles. Thus, the liquid columns observed in **Fig. 1b** are not formed due to a change in micelle morphology. Inspection of the silica-Span micellar solution interface reveals that the sample from the silica dispersion has a different structure than the one formed from DI water (**Fig. 2a. 8'**). In addition to the generated micro-scale droplets, we notice the coexistence of interconnected zones of oil and microemulsion-rich phases throughout the sample. In fact, the silica nanoparticle dispersion generates a bicontinuous phase that can be a new mechanism for generating stable liquid columns. The formation of the bicontinuous phase, and consequently liquid columns, is also observed at a lower Span

concentration of 10 wt.% (Supporting information, section IV).

The time evolution of the dark zone at the surface of the aqueous droplet, normalized by the droplet surface area, and denoted (A_n), at each time step is plotted in **Fig. 2c** (black for DI water and red for a 4.0 wt.% silica dispersion). At the interface of the DI water droplet, the fractional change in the area of the dark zone is generated at a rate of $\sim 0.01 \text{ min}^{-1}$ over 40 minutes, after which it decreases. The inset panel in **Fig. 2c** shows A_n from 1 to 24 hours, where it decreases to less than 0.1 for the case of DI water. The rate of bicontinuous phase formation is $\sim 0.1 \text{ min}^{-1}$ at silica dispersion-micellar solution interfaces, and reaches a plateau after ~ 4 minutes. The stability of the bicontinuous structures generated from a nanoparticle dispersion might be due to the presence of nanoparticles at the oil-water interface.

The interfacial tension (γ) of DI water and 20.0 wt.% Span micellar solution is $\sim 4 \text{ mN/m}$ initially, and decreases to $\sim 2 \text{ mN/m}$ after 30 minutes. In contrast, for a 4.0 wt.% silica dispersion and 20.0 wt.% Span micellar solution, γ is initially one order of magnitude lower ($\sim 0.16 \text{ mN/m}$) than that of DI water and reaches equilibrium ($\sim 0.08 \text{ mN/m}$) after about 2 minutes (**Fig. 2d,e**). The low values of interfacial tension of the silica dispersion can be the driving force for the rapid interfacial expansion and the formation of bicontinuous structures.

Figure 2: Spontaneous formation of interfacial materials. Bottom view images of the changes over time for a (a) DI water droplet and (b) 4.0 wt.% silica dispersion droplet in 20.0 wt.% Span micellar solution (scale bars = $500 \mu\text{m}$). Cryo-SEM images of the interfacial materials generated from DI water and a 4.0 wt.% silica nanoparticle dispersion after 24 hours are shown in (a. 7 – 8) and (b. 7' – 8'). In the sample generated from DI water (a. 7 – 8), a microemulsion zone containing submicrometer water droplets is formed. In the sample formed from the silica dispersion (b. 7' – 8'), interconnected structures of oil and microemulsion phases are formed uniformly throughout the sample. In the cryo-SEM images, the dark and light gray colors represent, respectively, oil and aqueous phases, while the nanoparticles are not visible. (c) Rate of bicontinuous phase formation. The surface area of the bicontinuous structures divided by the total surface area of the droplet is defined as A_n and plotted over 60 minutes.

Figure 2: The data points of the DI water droplet and 4.0 wt.% silica dispersion droplet are shown in black and red, respectively. The slope of initial regime in each case represents the rate of bicontinuous phase formation. The inset of the figure shows A_n over 24 hours. Dynamic interfacial tension (γ) of **(d)** DI water-20.0 wt.% Span micellar solution and **(e)** 4.0 wt.% silica dispersion-20.0 wt.% Span micellar solution. γ of DI water decreases slowly over time while γ of the silica dispersion remains constant after 2 minutes.

3.3 Universality of in-situ emulsification triggered liquid columns

To unravel the general conditions for the generation of liquid columns, we analyze different times scales of the process. The residence time, $t_R = L/U$, is defined as the time elapsed from the injection to the time the injected fluid reaches the bottom of container, where U is the injection speed and L is the distance between the nozzle tip and the container base. We hypothesize that liquid columns are generated when $t_E < t_R < t_D$, where t_E and t_D are the emulsification and diffusion times, respectively. This criterion, as indicated schematically in **Fig. 3a**, suggests that the liquid columns are formed when emulsions are generated within the time frame of an experiment but do not diffuse from the oil-water interface into the bulk oil. To organize a characterization of the dynamics, we define two dimensionless parameters, representing the relative importance of residence time and diffusion time scales to that of emulsification, as the convection Damköhler ($Da_C = t_R/t_E$) and diffusion Damköhler ($Da_D = t_D/t_E$) numbers.

First, we estimate the emulsification and diffusion times for a set of experiments where flow regime transitions occur, i.e., BOAS to column and column to connected, by increasing

the injection speed (**Fig. S16**). The BOAS regime appears at the longest residence times, meaning that emulsions are generated in this regime and diffuse from the interface (**Fig. 3a. 1**). Thus, the transition from the BOAS to the column regime is assumed to estimate the diffusion time. The connected regime emerges at the shortest residence times, where emulsions are not formed within the time frame of the experiment (**Fig. 3a. 3**). Hence, the transition from column to connected is defined as the emulsification time (**Table S1**).

The experimentally defined diffusion times in **Table S1** increase upon increasing the micellar solution viscosity (**Fig. 3b**, left and bottom axes in blue). This response is consistent with the Stokes-Einstein theory for diffusion in solution, where the diffusion time is a linear function of the medium viscosity ($t_D \sim \mu$) [30, 31] (Supporting information, section VI.1).

A plot of emulsification time in **Fig. 3b** (right and top axes in red) shows that in systems with $\gamma_{eq} < 0.6$ mN/m, the emulsification time is 0.2-0.5 s, independent of the interfacial tension value. In contrast, in systems with $\gamma_{eq} \geq 0.6$ mN/m, the emulsification time is a linear function of γ_{eq} . The equilibrium interfacial tension value is the key factor that controls the spontaneous emulsification process, driving the system toward equilibrium [32]. Hence, the emulsification time can be estimated as $t_E \sim \gamma_{eq}$ (Supporting information, section VI.1).

The convection and diffusion Damköhler numbers are calculated for a wide range of silica and Span concentrations and inner and outer fluid viscosities (**Figs. S2-S5, S14, and S16**) based on the time scale analysis in **Fig. 3b**. A plot of Da_C versus Da_D in **Fig. 3c** reveals that stable liquid columns are generated for $0.5 \leq Da_C < Da_D$, which verifies the hypothesized criterion. The coupling effect of emulsification kinetics (Da_C , Da_D) and hydrodynamics on the flow regimes are plotted in a three-dimensional phase diagram of $(Da_C - Da_D - Oh^2)$ in **Fig. 3d**, where the

149 Ohnesorge number, $Oh = \mu_i / \sqrt{\rho_i \gamma d_i}$, is a material property-related nondimensional number
150 representing the viscous to inertia and surface tension forces and is calculated based on the
151 inner phase viscosity (μ_i) and density (ρ_i), and d_i is the inner diameter of the needle. The
152 results in **Fig. 3d** categorize the four flow regimes observed in **Fig. 1** where the zone of stable
153 liquid columns is highlighted in green.

Figure 3: Dimensional analysis of the flow regimes. **(a)** Schematic of the flow regime transition from BOAS to column and connected. **(a.1)** The residence time is longer than the diffusion time. Emulsions are formed at the interface and diffuse to the bulk. **(a.2)** The residence time is longer than the emulsification time and shorter than the diffusion time. Thus, emulsions are generated and remain at the interface. **(a.3)** The residence time is shorter than the emulsification time, so that there is not enough emulsion at the interface to stabilize the liquid filaments. **(b)** Diffusion time, t_D (left and bottom axis in blue), and emulsification time, t_E (right and top axis in red), obtained from the flow regime transitions in (**Fig. S16**). The slope of lines are $31.5 \text{ m.s}^2/\text{kg}$ and $11.2 \text{ s}^3/\text{g}$, respectively. **(c)** Relative importance of diffusion and emulsification time scales as depicted by the diffusion (Da_D) and convection (Da_C) Damköhler numbers.

Figure 3: (d) 3D phase diagram of the flow regimes by considering the properties of the inner fluid. The highlighted zone in green shows the region of liquid column formation.

3.4 Liquid column characteristics and applications

The stability of liquid filaments during continuous injection was shown in **Fig. 1**. We also test their stability and durability after the injection has ceased. The 4.0 wt.% silica dispersion is injected in 20.0 wt.% micellar solution forming a stable column. Once the injection is stopped, the liquid inside the column drains immediately leaving a wrinkled tube skin. The generated emulsion phase forms an elastic skin keeping the structure of the column intact. Upon re-injecting the liquid, the column is restored to its original shape (**Fig. 4a** and Supporting Movie 5). The cycle of injection then stopping flow is repeated three times and can be further continued without observing any thread deterioration.

Moreover, the silica dispersion is loaded into a micro-pipette (volume 10 μl) and liquid letters with sharp and rounded edges are manually printed in the micellar solution (**Fig. 4b**). A high resolution microscopic image of a printed letter shows the presence of the bicontinuous phase of oil and microemulsions at the interface of the letter, which maintains the integrity of the structure. The long term stability of the printed structures, calculated by measuring the surface area of each printed texture (S) divided by its initial surface area (S_i), is plotted in **Fig. 4b**. The printed structures remain stable up to two months without losing their sharpness (**Fig. S18**).

Next, a slice (1/4) of a silica dispersion droplet at three different time steps is shown in **Fig. 4c**. Initially, the mixed green-black zones (bicontinuous phase) are only formed at the top and bottom of the droplet, which are in direct contact with the micellar solution. Over time the thickness of the emulsion phase increases, indicating that the emulsification advances into the depth of the droplet.

We also analyze the penetration depth of the bicontinuous structures inside the printed textures. The internal structures of the aqueous droplets previously shown in **Fig. 2a,b** are captured using confocal microscopy by scanning from the bottom to the top of the droplet in one micrometer steps (**Fig. S19**). **Fig. 4d** illustrates the area covered by the bicontinuous phase inside the silica droplet over 60 minutes at 6 time intervals. The inset images labeled as 1, 2, and 3 show the selected z stack at $z = 0, 100$ and $200 \mu\text{m}$ at the first time interval. The asterisk ($\star$) represents the selected images at the last time interval (50 – 60 minutes). The intensity of the bicontinuous phase in the center increases from 0 to 0.4 in 60 minutes, indicating the emulsification penetrates into the silica droplet. The penetration length of emulsions is proportional to the square root of time suggesting that the emulsion penetration is a diffusion dominated process (**Fig. S22**, right axis in blue).

The spatiotemporal 4D images of a silica drop deposited in the micellar solution provide information about the depth and rate at which the bicontinuous phase advances inside the silica drop and verify the formation of a spongy texture. Thus, a silica dispersion can be used as an ideal ink to create porous all-in-liquid materials.

Finally, a tortuous channel of silica dispersion is printed manually (the same method used for printing liquid letters) in Span micellar solution. Then, the printed channel is punched

by the tip of a second micropipette and 10 μ l of dyed DI water (yellow) is injected (**Fig.**
4e and Supporting Movie 6). The injected aqueous phase follows the pathway of the printed
texture without disintegrating the channel's structure and the elastic interfacial layer. Note that
the printed emulsions are continuously rejuvenated if part of the interfacial layer is ruptured
or damaged. Hence, the present approach for creating all-in-liquid materials offers a new
paradigm for in-liquid emulsion printing and liquid-based lab-on-chip techniques. We also
show the similarity, although different in length scales, between tube sponges in the oceans and
spongy liquid columns in **Fig. 4f**.

Figure 4: Applications of stable liquid filaments. **(a)** The stability of a liquid column during the injection-pause cycles. The outer diameter of the needle is 500 μm . **(b)** Printing liquid letters and their stability over two months. The surface area of each letter (S) is divided by its initial surface area (S_i) and plotted as a function of time. The error bars show the average change in surface area of 20 printed letters. The inset shows the printed letters (scale bar is 1 mm) and the formation of bicontinuous structures on the surface of the letters.

Figure 4: **(c)** 3D confocal images that show the formation of bicontinuous structures and their advancement in depth over time for 4.0 wt.% silica dispersion droplet in 20.0 wt.% Span micellar solution. Green and back colors represent silica dispersion and oil phases, respectively. The shade of green-black color indicates formation of emulsions and bicontinuous structures. The scale bar is 500 μm . **(d)** Confocal images are captured from the bottom ($z = 0$) to the top ($z = 200 \mu m$) of the droplet with a resolution of 1 μm in depth and 2 μm in the x-y plane at 10 minutes time intervals. Axes show time intervals, location in z, and surface coverage of the bicontinuous structures. **(e)** Injection of DI water (yellow) into the hand-printed silica dispersion channel. **(f)** Similarities between (i) tube sponges in oceans and (ii) spongy liquid columns. The image in (i) is taken from <https://reefguide.org/pixhtml/yellowtube10.html>. The yellow tube sponge is relatively large and it can grow up to 1 m in length. The scale bar in (ii) represents 1 cm.

4 Conclusion

In summary, we have demonstrated a strategy to print, all-in-liquid, porous materials by rapidly creating an emulsion zone that is locked at the oil-water interface. Distinct from previous approaches that rely on nanoparticle-surfactant jamming, which cannot create a porous structure, the discovery of such an in-situ emulsification mechanism dramatically upgrades our capability to print liquids consisting of many small droplets in a single step. The silica dispersion filaments are stabilized at Weber numbers two orders of magnitude smaller than unity due to

208 the rapid formation of emulsions at the interface and the slow diffusion of emulsions from the
209 interface to the bulk phase. The generality of our approach will open a new avenue for a wide
210 range of applications from energy storage [4,33] , due to their highly interconnected structures
211 that can be created spontaneously in large volumes with minimal input energy, high surface-to-
212 volume ratios, and the arrest of silica nanoparticles at the extended emulsion droplet surfaces,
213 to liquid-based lab-on-a-chip devices [12].

214 Previous research on the formation of liquid filaments for 3D printing in micellar solutions
215 is limited to the ionic surfactant-fatty acid systems. A gel phase is generated at the interface by
216 a change in the morphology of micelles from spherical to lamella, stabilizing liquid filaments of
217 surfactant solutions in oleic acid [9,27]. The developed approach in the present work differs from
218 studies on the ionic surfactant-fatty acid systems as the morphology of Span micelles remains
219 unchanged. Stable liquid columns are generated due to the in-situ formation of emulsion-
220 based interfacial layers. The silica-doped interfacial materials attain unique features where
221 (i) a column with elastic porous walls is formed and (ii) the printed structures in the oil
222 phase exhibit long-term stability on the order of months. The proposed technique offers great
223 flexibility for encapsulating different hydrophobic and hydrophilic cargoes inside the printed
224 structure and the surrounding medium, enabling the functionalization of a printed network
225 of droplets for tissue engineering [1] and addressing the challenge of delivery of incompatible
226 materials in biomedical applications [34–36]. It also creates porous structures for a wide range
227 of applications that require interactions between a printed structure and a liquid medium.

5 Method and Material

5.1 Materials

A 40 wt.% Ludox silica dispersion (HS 40, Sigma) is used as the concentrated source of nanoparticles. Silica nanoparticles in the dispersion are spherical with an average diameter of 7.9 ± 0.1 nm. The silica dispersion contains sodium counter ion with the concentration of < 0.08 % [37]. Sorbitan monooleate (Span 80, Sigma) is used as an oil soluble non-ionic surfactant. Span 80 has molecular weight of 428.60 g/mol and the hydrophilic-lipophilic balance (HLB) of 4.3. We use a sample of mineral oil (Drakeol 35, $\rho = 0.876$ g/cm³, $\mu = 135$ mPa.s) as the oil phase. For a few sets of experiments, minerals oils with different viscosities $\mu = 30$ mPa.s and $\mu = 1000$ mPa.s are used. A water-based fluorescent color (Cole-Parmer, UZ-00298-19) is used to stain the aqueous phase. All products are used as received without further purification. Unless otherwise stated, the HS silica dispersion, Drakeol mineral oil ($\mu = 135$ mPa.s, Span 80, and Span 80 dissolved in Drakeol mineral oil are referred to, respectively, as silica dispersion, oil phase, Span, and micellar solution in the entire manuscript.

5.2 Silica dispersion preparation

DIwater (Direct-Q, Millipore Sigma) is added to the concentrated silica dispersion to reach the desired concentrations of 1.0 ($\rho_i = 1.003$ g/cm³, $\mu_i = 1.0$ mPa.s), 2.0 ($\rho_i = 1.009$ g/cm³, $\mu_i = 1.1$ mPa.s), and 4.0 ($\rho_i = 1.027$ g/cm³, $\mu_i = 1.2$ mPa.s) wt.%. Samples are homogenized in an ultra sonic bath (Isonic P4830) for 10 minutes.

5.3 Micellar solution preparation

Span is dissolved in mineral oil at concentrations of 1.0, 5.0, 10.0, 20.0, and 40.0 wt.%. Samples are sonicated in the bath for 30 minutes.

5.4 Experimental set-up

Liquid columns are generated in a vertical rectangular cell ($2\text{ cm} \times 4\text{ cm} \times 1\text{ cm}$) through a needle with the outer diameter of $500\text{ }\mu\text{m}$ and the inner diameter of $400\text{ }\mu\text{m}$.

5.5 Spinning drop tensiometer (SDT)

The dynamic interfacial tensions (IFT) of the nanoparticle dispersions - micellar solutions are measured using a spinning drop tensiometer (SDT, Kruss). The glass capillary is filled with the aqueous phase and an oil drop is placed at the top of the plastic cap. The spinning rate is in the range of $6000 - 8000\text{ rpm}$, and data are recorded for 2000 seconds. Vonnegut's equations is used to obtain the interfacial tension values for each sample. $\gamma = (\rho_{\text{aqueous phase}} - \rho_{\text{micellar solution}}) \omega^2 R^3 / 4$, where ω and R are, respectively, the spinning rate and the radius of the liquid cylinder.

5.6 Density measurement

The densities of the aqueous phases (silica dispersions) are measured using Density2Go (Mettler Toledo) and the densities of the oil phases (micellar solutions) are measured by DMA 35 (Anton Paar).

5.7 Viscosity measurements

The viscosities of the aqueous phases (silica dispersions), micellar solutions, and microemulsions (bicontinuous phase) are measured using Discovery Hybrid Rheometer (DHR-2, TA Instruments).

5.8 Confocal laser scanning microscopy (CLSM)

Images are captured with 4X (CFI Plan Apo Lambda, Nikon, resolution of $6.2\ \mu\text{m}/\text{pixel}$) and 10X (CFI Plan Flour, Nikon, resolution of $2.3\ \mu\text{m}/\text{pixel}$) magnifications using confocal laser scanning microscopy (Nikon A1R). The laser power is set at 10 – 15 mW, and the pinhole is fixed at 1.2 AU for all images. We use 488 nm (FITC) and 561 nm (TRITC) laser emissions to detect the oil phase and silica dispersion, respectively.

5.9 Cryogenic-scanning electron microscopy (Cryo-SEM)

A variable pressure environmental field emission scanning electron microscope (FEI Quanta 250 FEG) coupled with a Gatan Alto2500 cryo-transfer system is used to capture images of the emulsions. Samples are freeze-dried in liquid nitrogen before the imaging.

5.10 Bottle experiments

3 ml of an aqueous phase (DI water or silica nanoparticle dispersions) is poured into a glass vial (20 ml) and 3 ml of an oil phase is gently added at the top of the aqueous phase using a micro-pipette. Emulsification/bicontinuous phase formation starts spontaneously without shaking, stirring, or homogenizing.

5.11 Image analysis

Image Fiji software is used to analyze the color camera and confocal images and calculate porosity of 3D bicontinuous structures. The droplet size is measured using *Analyze Particle* modulus. 3D images are imported as a sequence of z-stack images and reconstructed using the *3D Objects Counter* modulus. Then, the porosity is calculated by measuring the void volume of each image divided by the total volume.

5.12 Fourier transform analysis

The time series images of the injection of aqueous phase into micellar solutions (**Figures S1-4**) at different concentrations of nanoparticles and surfactants and the injection flow rate are binarized with an appropriate threshold value in image Fiji software. The power spectrum is calculated at each y (location along the column) from the summation of threshold pixels in x direction. The data is obtained from plot profile. Then, the average power spectrum is calculated using 1D Fourier analysis in Matlab.

Note. All experiments are conducted at atmospheric pressure (88.4 ± 0.8 kPa) and temperature (21 ± 0.5 °C). IFT, density, and viscosity experiments are repeated at least three times. Emulsion samples are generated at least ten times to confirm the reproducibility of the spontaneous formation of bicontinuous structures. Image analysis is repeated four times for each sample.

Data availability. All raw data of DLS measurements are provided in graphs as supplemental materials. All raw data for interfacial measurements will be provided in numerical forms in a spreadsheet upon request. A full series of CLSM images captured can be provided when

305 required.

306 References

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6 Author contributions

P.B. conceived the main idea for the study, designed and conducted the experiments, and prepared the figures. P.B. and S.H.H. performed most of the result interpretation and wrote the first draft. All authors discussed results, contributed ideas for mechanism interpretation, commented on the manuscript, and edited the text.

417 **7 Competing interests**

418 The authors declare no competing interests.

419 **8 Materials and Correspondence**

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