

Electronic Supplementary Information (ESI)

A Simple Microfluidic Probe of Nanoparticle Suspension Stability

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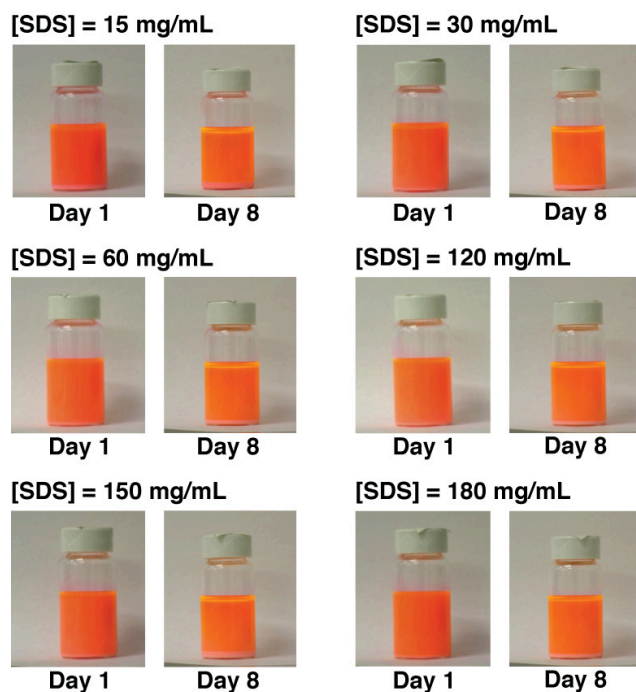


Figure S1. Photographs showing results of a titration experiment whereby a 7 mL aliquot of aqueous rhodamine 6G (0.5 mg/mL) solution was added to 7 mL of a series of 1 vol% Al₂O₃ suspensions with increasing SDS concentration. In all cases, sedimentation at the bottom of the container became evident within a few minutes after adding the tracer. We did not apply stirring or ultrasonication in these titration experiments in an effort to mimic phenomena in the microchannel environment

Table S1. Summary of previous zeta potential measurements in aqueous alumina suspensions.

pH	Loading/particle size (nm)	Zeta Potential (mV)	Dispersant	Salt or Ionic Compound	Key Observations	Ref.
3 – 10	– / 120	-50 to -30 mV	SDS	0.001 M KNO ₃	Due to adsorption of anionic SDS onto alumina, negative Zeta potential was measured and remained fairly stable (-+7mV)	1
2 – 11	0.02 wt% / < 1000	-40 to 40	SDS Dodecylamine chloride (DDA)	0.001 M KCl	SDS addition made zeta potential positive to negative and DDA has almost no effect on the zeta potential of alumina at pH < 9	2
5.2	10 mg/ml / 2500	-30 to 30	SDS PVcA (Poly(1-vinylpyrrolidone-co-acrylic acid))	–	The positive zeta potentials decreased to zero and reached some negative zeta potentials with the SDS concentration	3
6.5	5 g / 300	-70 to 40	SDS	0.1 M NaCl	The decrease in Zeta potential of alumina as a function of SDS concentration. When SDS concentration is higher than 0.001 M, complete surface coverage	4
3 – 11	0.05 g / 72	-80 to 40	TX-100 SDS	0.001 M NaCl	Carboxymethylcellulose-alumina system Presence of surfactants decreases zeta potential and shift p <i>H</i> _{iep} from 7.6 to 6 or 5	5
2 – 12	0.01 wt% / 600	-50 to 50	Anionic Ammonium polycarboxylate	–	Presence of surfactants decreases zeta potential and shift p <i>H</i> _{iep} from 9.1 to 6.3 and 3.4	6
4 – 11	– / 100	-30 to 60	–	–	p <i>H</i> _{iep} is basic for alumina (~ 9.1)	7

(p*H*_{iep} indicates the pH value where surface concentration of H⁺ and OH⁻ are equal)

Table S2. Measured pH of aqueous dye solutions and suspensions.

Solution Composition (concentrations in units of mg/mL)	Measured pH							Mean	Std. Dev.
	1	2	3	4	5	6			
Rh 6G (0.1)	4.77	4.75	5.08	4.73	4.74	4.78	4.81	0.13	
Rh 6G (0.5)	5.00	5.09	5.12	5.18	5.13	5.14	5.11	0.06	
Rose Bengal (5)	5.51	5.50	5.58	5.49	5.53	5.55	5.53	0.03	
Al₂O₃	4.89	4.60	5.08	4.71	4.78	4.74	4.80	0.17	
Al₂O₃-SDS (15)	7.19	7.35	7.56	7.08	6.99	7.44	7.27	0.22	
Al₂O₃-SDS (120)	7.71	7.83	7.37	7.80	7.45	7.79	7.66	0.20	
Al₂O₃-SDS (15)-Rh 6G (0.1)	8.17	7.78	8.12	7.74	8.17	7.77	7.96	0.21	
Al₂O₃-SDS (15)-Rh 6G (0.5)	7.56	8.08	8.18	7.53	8.08	8.21	7.94	0.31	
Al₂O₃-SDS (15)-Rose Bengal (5)	7.39	7.26	7.30	7.31	7.12	7.14	7.25	0.10	

All suspensions contain Al₂O₃ nanoparticles at 0.25 vol% solution. Rhodamine 6G and Rose Bengal concentrations were 0.1, 0.5 and 5 mg/mL, respectively. The SDS concentration was 15 and 120 mg/mL. These concentrations are specified in parentheses beside each compound.

Table S3. Two independent series of zeta potential measurements performed in a standard 10 wt% Ludox TM-50 colloidal silica suspension in 0.01 M KCl.

Measurement series	Zeta Potential (mV)										Mean	Std. Dev.
	1	2	3	4	5	6	7	8	9	10		
1	-52.31	-51.68	-47.17	-54.43	-47.68	-48.99	-49.85	-50.20	-45.21	-49.49	-49.70	2.68
2	-51.93	-54.76	-46.27	-52.78	-51.74	-50.60	-55.88	-51.70	-50.57	-51.69	-51.79	2.58

Average pH of suspensions was 9.30.

Table S4. Zeta potential measurements of the nanoparticle suspensions.

Suspension Composition	Zeta Potential (mV)										Mean	Std. Dev.
	1	2	3	4	5	6	7	8	9	10		
Al₂O₃	45.6	51.13	44.82	46.5	46.88	52.33	48.41	47.75	40.11	50.55	47.41	3.55
Al₂O₃-SDS (15)	-43.66	-44.92	-40	-46.78	-47.75	-51.10	-48.76	-42.95	-44.37	-39.49	-44.98	3.71
Al₂O₃-SDS (120)	-49.78	-46.28	-51.73	-38.04	-41.97	-56.65	-50.51	-47.68	-42.55	-63.58	-48.88	7.47
Al₂O₃-SDS (15) - Rh 6G (0.1)	-19.20	-17.19	-15.76	-18.77	-20.50	-18.21	-13.98	-15.97	-20.02	-17.19	-17.68	2.05
Al₂O₃-SDS (15) - Rh 6G (0.5)	-15.71	-13.72	-19.22	-11.80	-18.34	-10.01	-10.03	-12.70	-15.60	-16.22	-14.34	3.23
Al₂O₃-SDS (15) - Rose Bengal (5)	-42.78	-39.26	-40.21	-42.48	-47.80	-37.24	-44.31	-35.1	-37.37	-33.47	-40.00	4.41

All suspensions contain 0.25 vol% Al₂O₃ nanoparticles. Rhodamine 6G and Rose Bengal concentrations were 0.1, 0.5 and 5 mg/mL, respectively. The SDS concentration was 15 and 120 mg/mL. These concentrations are specified in parentheses beside each compound.

Table S5. Particle sizes obtained using DLS.

Suspension Composition	Particle Size (nm)							
	1	2	3	4	5	6	Mean	Std. Dev.
Al₂O₃	176.3	160.6	183	171.4	148.8	141.5	163.60	16.22
Al₂O₃-SDS (15)	162.2	150.7	165.8	157.4	169.9	160.1	161.02	6.69
Al₂O₃-SDS (120)	193	152	149.9	172.9	155.3	149.7	162.13	17.45
Al₂O₃-SDS (15) -Rh 6G (0.1)	181.8	172.4	200.3	168.4	174.1	160.8	176.30	13.63
Al₂O₃-SDS (15) -Rh 6G (0.5)	184.1	157.9	169	170.7	168.7	184.5	172.48	10.21
Al₂O₃-SDS (15) -Rose Bengal (5)	168.4	153.9	148.1	176.9	168.1	152.7	161.35	11.34

All suspensions contain Al₂O₃ nanoparticles at 0.02 vol% solution. At this dilution, rhodamine 6G and Rose Bengal concentrations were ~ 0.0087, 0.043 and 0.43 mg/mL, respectively. The SDS concentrations were ~1.3 and 10.4 mg/mL, respectively at the 15 and 120 mg/mL bulk conditions specified in parentheses beside each compound.

Microdevice Design and Assembly

Microchannels were constructed in poly(dimethyl siloxane) (PDMS) using standard soft lithography methods. Briefly, Y-shaped microchannel patterns (50 μm tall, 500 μm wide, 2.7 cm long from the junction of the two inlets to the downstream outlet) were designed using AutoCAD 2006 software (Autodesk, Inc.) and printed on transparency film with a 20,320 dpi (Fineline Imaging, Colorado Springs, CO). Master molds were constructed by spin coating thick

photoresist (SU-8 2025; MicroChem Corp.) onto the surface of a silicon wafer at 500 rpm for 10 s with an acceleration of 100 rpm/s followed by 1,460 rpm for 30 s with an acceleration of 300 rpm/s, after which the wafer was baked at 65 °C for 3 min followed by 95 °C for 8 min. The microchannel patterns were then transferred by exposing the wafers to UV light through the transparency film using a mask aligner (Quintel Q-4000IR), after which the unexposed photoresist was removed using SU-8 developer solution. This process yielded 50 μm feature heights (corresponding to the depth of the cast microchannels) as determined using a stylus profilometer (Dektak 3; Veeco Instruments, Inc.).

The SU-8 master molds were used to cast microchannels in PDMS (Sylgard™ 184; Dow Corning Corporation). The base and crosslinker were mixed in a 10:1 ratio by volume followed by degassing under vacuum for approximately 15 min to remove trapped air bubbles. The mixture was then poured over the master mold and cured at 80 °C for approximately 2 h. The crosslinked PDMS was then peeled away and access holes were punched at the endpoints (inlets and outlet) of the microchannel using a sharpened syringe needle (Cat No. 305196; Becton, Dickinson and Company). The PDMS structures were bonded to 75 x 50 mm, 1 mm thick glass microscope slides (Cat No. 12-550C; Fisher Scientific, Pittsburgh, PA) to produce enclosed microchannels after treating both surfaces in plasma using a reactive ion etcher (Model CS-1701; March Plasma Systems) for 30 s under the following conditions: O₂ gas flow of 4 sccm, electric power of 25 W, base pressure of 80 mTorr, and temperature of 0 °C. Finally, fluidic connections were made by inserting 0.38 mm i.d., 1.09 mm o.d. polyethylene tubing (Intramedic™ (Non-Sterile), Cat. No. 427406; Becton, Dickinson and Company) into the access holes. Flows at rates ranging from 0.05 to 0.25 mL/min were generated using a syringe pump (Model KDS-230, kd Scientific Inc.).

Flow Visualization and Data Analysis

Interfacial aggregation studies were carried out by imaging parallel co-flowing streams containing dye and suspended nanoparticles, respectively, using a Zeiss LSM 5 Pascal Confocal Scanning Microscope with a Zeiss Plan-Neofluar 10X/0.3 numerical aperture objective interfaced with Canon PowerShot 640 digital camera (4x zoom) and Zeiss LSM 5 software (Release 3.2). During imaging, a halogen lamp (3.8 V) was used as a light source in transmitted light mode with BF filter and condenser aperture was adjusted to 0.6706. Images were recorded at multiple downstream locations from the microchannel inlet and assembled into a composite picture using Adobe Photoshop. The downstream location x^* corresponding to the onset of instability in the aggregation pattern (Fig. 1a) was chosen to be the point where the interfacial aggregation line began to exceed 38 μm in width.

Preparation of Nanoparticle Suspensions

Alumina suspensions were prepared at final concentrations ranging from 0.25 to 1 vol% by dilution in deionized water from a commercially available 15.4 wt% Al₂O₃ solution (Nanomyte™; NEI Corporation) specially ordered to include no stabilizing surfactant. This formulation was selected because it provided the best tradeoff between stability against sedimentation and the ability to control the composition and amount of surfactant added to stabilize the suspension after addition of dyes. Suspension stability was particularly important in our complexation experiments done in microchannel because total setup and running times of order 1 h were required owing to the low flow rates imposed. The nanoparticle suspensions were prepared by adding surfactant (sodium dodecyl sulfate (SDS), Cat. No. BP166; Fisher Scientific)

to an appropriate dilution of the as supplied commercial nanofluid. Nanoparticle volume percentages were determined from the suspension weight percentages as follows

$$\phi_v = \frac{1}{\left(\frac{100}{\phi_m}\right)\left(\frac{\rho_p}{\rho_w}\right)+1} \times 100(\%)$$

where ρ_p and ρ_w are the densities of alumina (3.97 g/cm^3) and water ($\sim 1 \text{ g/cm}^3$) respectively, and ϕ_v and ϕ_m are the volume and weight percentage of the suspensions.

A SDS concentration of 15 mg/mL was chosen to be well above the critical micelle concentration of 2.5 mg/mL. Suspensions were mixed for 5 h using a magnetic stirrer, followed by 5 h of ultrasonic agitation in an ultrasonic cleaner (Model 3510DTH; Branson Ultrasonics Corp.), followed by 30 min of agitation using a probe sonicator (Vibracell VCX 750; Sonics & Materials Inc.) to ensure homogeneity and stability.⁸

Suspensions containing fluorescent tracers were prepared by adding dye during the mixing process. When necessary, sonication and mixing times were doubled to counteract the increased tendency toward sedimentation due to interactions between the dye, surfactant, and nanoparticles. Particle-free aqueous dye solutions of rhodamine 6G (Cat. No. R4127; Sigma-Aldrich) were prepared by dissolving the powdered dye in water to yield a final concentration of 0.5 mg/mL. Methanol (5 vol. %, Fisher A412-1) was also added in aqueous solution to solubilize the dye. Similarly, Rose Bengal dye powder (sodium salt, Cat. No. R3877; Sigma-Aldrich) was dissolved in water to a concentration of 5 mg/mL. All particle-free dye solutions were mixed using a magnetic stirrer for 3 h, followed by 30 min of ultrasonic agitation in a Branson 3510DTH ultrasonic cleaner, followed by another 3 h of mixing with a magnetic stirrer. pH values of tracer dye containing suspensions were measured using a Chekmiter pH-25 meter (Corning Inc.).

Viscosity Measurements

Viscosities of the alumina suspensions ($\sim 0.5 \text{ mL}$ sample volume) were measured over a wide range of shear rate using a Paar Physica MCR 300 Modular Compact Rheometer at $25 \text{ }^\circ\text{C}$. The measuring system geometry was a parallel-plate set-up (CP 50-1, diameter: 50 mm, gap width: 0.05 mm, angle: 0.987 (Cat No: 79040, Anton Paar)). The instrument was programmed for constant temperature and equilibration followed by two-cycle shear in which the shear rate was increased from 10 to 500 s^{-1} and immediately decreased from 500 to 10 s^{-1} without a pause between up (forward) and down (backward) ramps. All rheological tests were done in triplicate. The temperature was controlled using a circulating water bath (*Lauda Model RE106*).

Thermal Conductivity Measurements

Thermal conductivity measurements were performed with a handheld thermal property analyzer (Model KD2-Pro, Decagon Devices, Inc.) using the 60 mm long by 1.3 mm diameter probe (KS-1). This device operates based on the transient hot wire method and is capable of measuring conductivities in the range from 0.02 to $2.00 \text{ W/m}\cdot\text{K}$ with an accuracy of $\pm 5\%$ or $0.01 \text{ W/m}\cdot\text{K}$ over a span of 0 to $50 \text{ }^\circ\text{C}$. The measurement consists of applying a 30 s heat pulse to

the probe, after which the temperature decay with time is recorded and related to the thermal properties of suspension. Alumina suspensions were prepared in larger quantities (180 mL) both with and without dye following the procedures described previously and placed in a glass beaker (5.6 cm i.d. by 8.5 cm length) and immersed in an isothermal bath (*Lauda Model RE106*) at 22.3 °C to minimize free convection. The free surface of the fluid sample was covered by a layer of light mineral oil (Cat. No. BP2629-1; Fisher Scientific) when to reduce surface tension effects in the vicinity of the probe, and the isothermal bath was switched off during the measurement to eliminate vibration. The probe was calibrated using glycerin and water standards, and consistently yielded results in good agreement with literature.⁹ The plotted data are averages of three independent measurements (at least 20 min elapsed between each measurement).

Dynamic Light Scattering (DLS) Measurements

Particle size distributions were characterized by DLS using a ZetaPALS instrument with a BI-9000AT correlator (Brookhaven Instruments Corp.). Samples containing 0.25 vol% alumina nanoparticles were diluted to a concentration of 0.02 vol%. During this process, surfactant (15 or 120 mg/mL) and dye concentrations (0.1, 0.5 or 5 mg/mL) were also diluted by the same amount (~ 1/12). Time-averaged particle size distributions were collected over an analysis period of at least 5 min at room temperature. Six separate measurements were acquired for each freshly prepared solution. The wavelength of the incident laser beam (λ) was 660 nm, and the detector angle (θ) was 90°. The autocorrelation functions were deconvoluted using the built-in non-negatively constrained least squares-multiple pass (NNLS) algorithm in order to obtain particle size distribution.

Zeta Potential Measurements

Zeta potential measurements were performed by phase analysis light scattering using a ZetaPALS analyzer (Brookhaven Instruments Corp.). The analyzer was equipped with a 35 mW red diode laser operating at 660 nm. Default settings (dielectric constant, refractive index and viscosity) were assumed to be the same as for water. The Smoluchowski approximation was used as a model for calculations. Samples containing 0.25 vol% alumina nanoparticles were placed in an acrylic cuvette, and 10 measurements were performed at 25 °C. Before testing our solutions, we prepared a standard suspension containing 10 wt% Ludox TM-50 colloidal silica (Cat. No. 420778, Sigma Aldrich) to check electrode sensitivity. Ionic strength was adjusted with 0.01M KCl.

TEM Characterization of Nanoparticle Suspensions

Transmission electron microscopy (TEM) images of the alumina samples were taken by high resolution analytical TEM instrument (JEOL JEM 2010). Prior to the measurement, the nanoparticle suspensions were deposited on a carbon film TEM grid (Ni mesh) and allowed to dry by evaporation under ambient conditions. The images were taken in high vacuum at ~room temperature. These micrographs reveal that the alumina nanoparticles have a spherical morphology with, characteristic particle sizes in the range of 10 – 100 nm (**Fig. S2**).

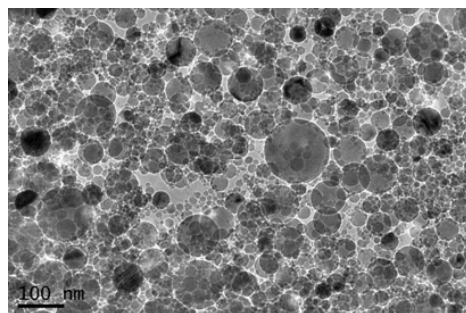


Figure S2. TEM micrograph of evaporatively dried alumina suspension (bar, 100 nm).

SEM Characterization of Deposited Nanoparticle Aggregates

Scanning electron microscopy (SEM) images of the aggregates deposited by microfluidic interfacial colloidal destabilization were obtained using a JEOL JSM-6400 at an accelerating voltage of 15 keV and 15 mm working distance. The JSM-6400 is equipped with a Princeton Gamma-Tech (PGT) EDS System. The aggregation experiment was conducted in a microchannel prepared using a thermoplastic elastomer substrate by soft lithography.¹⁰ The top (microchannel) and bottom (flat) parts were prepared from an elastomeric polystyrene-(polyethylene/polybutylene)-polystyrene (SEBS) triblock copolymer resin (Kraton G1657) and a 1 mm thick polycarbonate film, respectively. Master molds incorporating the Y shaped microchannel design were fabricated using printed circuit boards, and the pattern was imprinted by placing a slab of elastomer on top of a master mold that had been preheated to 120 °C on a hot plate. Within seconds, the elastomer begins to soften and can be gently pressed down by hand for several seconds to make uniform contact with the structures on the mold. After cooling and release, the solidified gel precisely replicates the shape of the structures on the master. Bonding can be achieved with polycarbonate surface by briefly heating the material at the bond interface to a temperature just below its softening point using a hot plate or handheld heat gun. This fabrication approach allows a static or low-pressure microfluidic network to be constructed, but the bond can be easily removed by peeling off the elastomer microchannel for subsequent SEM analysis. After disassembly, the flat polycarbonate film containing the deposited aggregates was dried at room temperature in an enclosed container, coated with a thin gold-palladium layer (500 Å) using a Hummer II sputter coater (Anatech), and subsequently was observed with SEM. The chemical composition was evaluated using high energy dispersive X-ray spectroscopy (EDS, JEOL JSM-6400). The micrographs depict the morphology of the deposited aggregates, and elemental analysis confirms that they are composed of alumina nanoparticles (**Fig. S3**).

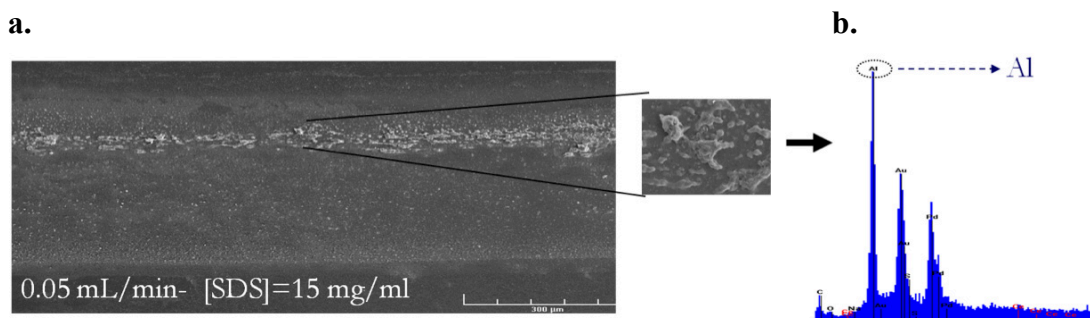


Figure S3. (a) SEM image of nanoparticle aggregates deposited on the microchannel floor at the interface between co-flowing streams. (b) EDX analysis of the aggregation zone. Highest peak corresponds to Al.

References

1. T. Gopal and J. B. Talbot, *J. Electrochem. Soc.*, 2006, **153**, G622-G625.
2. Y. Hu and J. Dai, *Miner. Eng.*, 2003, **16**, 1167-1172.
3. K. Sakagami, T. Yoshimura and K. Esumi, *Langmuir*, 2002, **18**, 6049-6053.
4. P. Chandar, P. Somasundaran and N. J. Turro, *J. Colloid. Interf. Sci.*, 1987, **117**, 31-46.
5. E. Grzadka, *Mater. Chem. Phys.*, 2011, **126**, 488-493.
6. B. P. Singh, R. Menchavez, C. Takai, M. Fuji and M. Takahashi, *J. Colloid Interf. Sci.*, 2005, **291**, 181-186.
7. F. J. Rubio-Hernandez, M. F. Ayucar-Rubio, J. F. Velazquez-Navarro and F. J. Galindo-Rosales, *J. Colloid. Interf. Sci.*, 2006, **298**, 967-972.
8. S. Ozturk, Y. A. Hassan and V. M. Ugaz, *Nano Lett.*, 2010, **10**, 665-671.
9. Vargaftik N B, Filippov L P, Tarzimanov A A and Totskii E E, *Handbook of Thermal Conductivity of Liquids and Gases*, CRC Press Boca Raton, 1994.
10. A. Sudarsan, J. Wang and V. Ugaz, *Anal. Chem.*, 2005, **77**, 5167-5173.