Electronic Supplementary Information (ESI)

Dispersion Forces Acting between Silica Particles across Water: Influence of Nanoscale Roughness

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Experimental

Materials. The experiments were carried out using spherical silica particles purchased from Bangslab Lab (USA). The manufacturer reports an average diameter of 5.2 μm as measured with a Coulter Counter. Prior to the experiments, the particles were heat-treated at temperatures of 1050, 1100, 1150 and 1200°C for 2 hours with a high-temperature furnace (Nabertherm, Germany).

Particle Size. The size of the silica spheres was measured by scanning electron microscope (SEM, JSM-6510LV, JEOL). Particles were spread on a silicon wafer of about 5×5 mm^2 area that was subsequently attached to the SEM support, gold coated at a partial pressure of 10 Pa during 30 s, and imaged. In case of heat-treated particles, the particles spread on the wafer and heated for 2 hours and then attached and imaged. About 50 particles were imaged, and the diameter of each particle was extracted with ImageJ software. The scale of the images was calibrated with 1 μm standard calibration grid (Ted Pella, Inc.). The coefficient of variation was about 1.5%, and this value is the same for all samples within experimental error.

Surface Roughness. The surface topography of the particles was characterized by AFM imaging. Images of the particles were acquired with a closed-loop AFM (MFP-3D, Asylum Research) mounted on an inverted optical microscope (Olympus IX70) in amplitude modulation mode. The particles were attached to the glass slide sealing the AFM fluid cell as follows. In case of heat-treated particles, the slide was cleaned by soaking it in piranha solution, which is a mixture of H_2SO_4 98% and H_2O_2 30% in a ratio 3 :1 for 20 min, rinsed with water, and dried under a stream of nitrogen. Subsequently, particles were spread onto a square quartz slides of 19 mm (Edmund Optics) and cleaned in air-plasma for 10 min, and then heat-treated for 2 hours. Extending the heat treatment to 3 hours had no noticeable effects on the results. The reverse side of the slide was then glued (Pattex 100% Repair Gel) onto the glass slide sealing the AFM cell. In case of untreated particles, the particles were glued directly on the slide with epoxy glue (Araldite 2000+) as follows. A few particles were spread on the glass slide and a drop of about 5μL of glue was deposited in their proximity. A cantilever was mounted in the AFM, dipped in the glue with the translation stage, and then used to draw few thin lines of glue on the glass slide. Then another cantilever, which was previously cleaned with air plasma for 5 min, was used to pick up some particles, they were placed on the glue stripes, and the glue was cured during 8 hours. Prior each experiment, the quartz or the glass slide was abundantly rinsed with ethanol and water, and after drying treated in air plasma for 20 min. The imaging was carried out in 10 mM KCl solution adjusted to pH 4.0 with HCl with silicon cantilevers (OMCL-AC240TS, Olympus) having a nominal tip radius <10 nm and a resonance frequency of about 110 kHz in air. Images were acquired with a scan rate of 0.2 μm/s, free oscillation amplitude (FOA) of about 10 nm, and a set point to around 90% of the FOA. The roughness was determined for an area of 1×1 μm^2 and averaged over 10 particles.

X-Ray Powder Diffraction. The effect of the heat-treatment on the particles was further analyzed with X-ray diffraction on a X-ray diffractometer (Empyrean, Panalytical) in transmission geometry using a focusing elliptical mirror ($CuK\alpha_1$, $CuK\alpha_2$ radiation). The powder was placed in a 0.8 mm glass capillary and data were collected in the 2θ-range from 3° to 55°, with a step of 0.013° and an exposure of 2400 s per step. The background coming from the glass capillary was subtracted by doing a measurement of an empty capillary.

Direct Force Measurements. Forces between the silica particles in KCl solutions were measured by the colloidal probe technique using the same AFM described above. The particles were attached to tip-less cantilevers and the substrate as follows. The cantilevers (MikroMasch, Tallin, Estonia) were cleaned in air plasma (PDC-32G, Harrick, New York) for 5 minutes. Few silica particles were placed on a glass slide and tiny drops of about 5 μL of glue (Araldite 2000+) were deposited in their proximity. The cantilever was mounted in the AFM, brought in contact with the drop of the glue with the translation stage, and a particle was picked up in this fashion. The same procedure described above was used to glue particles on the substrate. Prior to the measurements, the quartz slide and the probes with the attached particles were rinsed in pure water, then in ethanol, dried in air, and finally treated in air plasma for 20 min. The AFM fluid cell was mounted with the slide and the cantilever, thoroughly flushed with the respective electrolyte solution, and then closed. The experiments were carried out at a temperature of 22±2°C in KCl solutions in Milli-Q water (Millipore) adjusted to pH 4.0 by HCl. The attached particle was centered above another isolated particle on the substrate, and a precise alignment was achieved to an accuracy of about 100 nm by horizontal adjusting the AFM-piezos and by observing the interface fringes with the inverted optical microscope. Continuous monitoring of the experiment with the optical microscope also ensures that only forces between the particle attached to the cantilever and another attached to the substrate were recorded. Particle aggregates formed on the substrate were systematically avoided in the force measurements, as such aggregates could be easily recognized in the optical microscope. The forces were obtained by averaging about 150 approach and retraction cycles, which were accumulated with sampling rate of 5 kHz, a cycling frequency of 0.5 Hz and approach-retraction velocities of 300 nm/s. In order to determine the constant compliance and the zero distance in the force versus distance curve, we assumed zero separation when the load reaches and 1 nN/m. The separation distance has a precision of about 0.3 nm for each individual force curve, and is similar to procedures used previously. The cantilever deflection was converted into forces with the spring constant of the cantilever. The resulting force resolution is about 0.9 pN. The cantilever spring constants were obtained from its resonance frequency, quality factor, and its lateral dimensions, and they were in the range of 0.1–0.3 N/m. The spring constant determined in this fashion agreed with those determined from thermal fluctuations of the cantilever within 10%. The measured forces were finally normalized with the effective radius. The measurements were well reproducible to for different particle pairs, whereby the resulting Hamaker constants remained within about 10%. The small range of the forces also ensures that the presence the substrate does not influence the measured force profiles.

Table S1. Fitted double layer potentials at different salt concentrations for silica particles heated at different temperatures.

Heating Temperature (°C)	Salt Concentration (mM)	Diffuse Layer Potential ψ_D (mV)
1050	50	–6.40 ± 0.02
	≥ 500	0[a]
1150	50	–12.02 ± 0.02
	100	–7.13 ± 0.03
	≥ 250	0[a]
1200	50	–10.61 ± 0.04
	75	–9.97 ± 0.06
	77	–9.09 ± 0.05
	100	–7.73 ± 0.04
	120	–6.67 ± 0.03
	150	–5.23 ± 0.08
	≥ 300	0[a]

[a]The force profile becomes independent of the potential in the distance range considered, and the potential has been set to zero.

Table S2. Properties of silica particles, which were heat-treated at different temperatures, and comparison with the untreated ones.

Temperature (°C)	Average Radius[a] (µm)	Coefficient of Variation[a] (%)	RMS[b] (nm)	Correlation Length[c] (nm)	Hamaker Constant ($\times 10^{-21}$ J)
Untreated	2.49 ± 0.04	1.8	2.5 ± 0.3	19.6	0.07 ± 0.05
1050	2.19 ± 0.03	1.4	2.7 ± 0.3	13.7	0.27 ± 0.05
1100	2.20 ± 0.03	1.5	2.1 ± 0.2	15.7	0.47 ± 0.03
1150	2.19 ± 0.03	1.2	0.81 ± 0.09	13.7	1.6 ± 0.03
1200	2.21 ± 0.03	1.6	0.63 ± 0.07	29.3	2.4 ± 0.05

[a]From scanning electron microscopy. [b]From topographic AFM images. [c]The correlation length was obtained from the distance where the correlation function shown in Fig. S5 has decayed to 1/2.

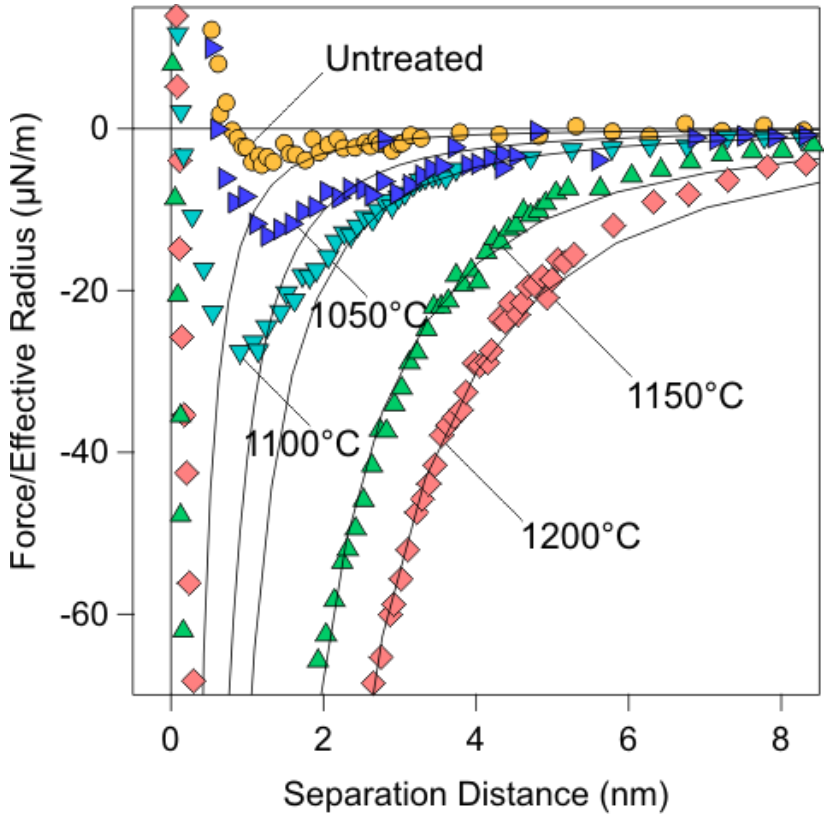

Figure S1. Measured forces versus the separation distance in 1.0 M KCl solution at pH 4.0 for different heating temperatures together with best fits with DLVO theory as described in the main text. The resulting diffuse layer potentials are given in Table S1.

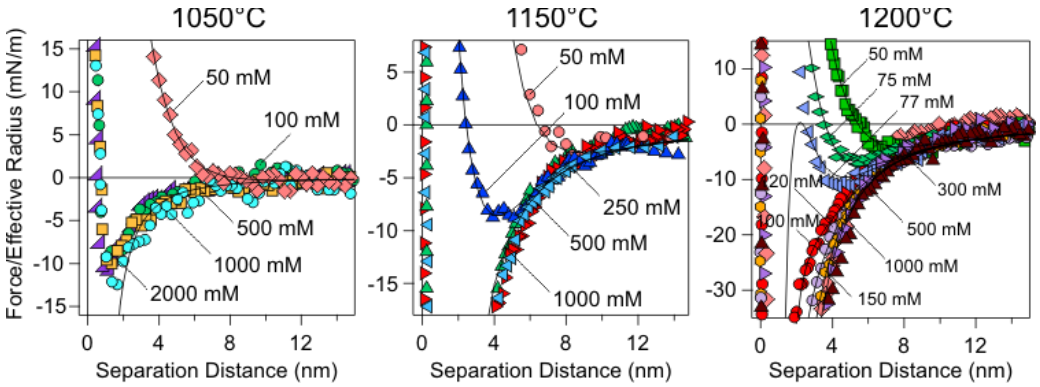

Figure S2. Measured forces versus the separation distances at different salt concentration at pH 4.0 with best fits with DLVO theory as described in the main text. The different subfigures refer to the different heating temperatures indicated.

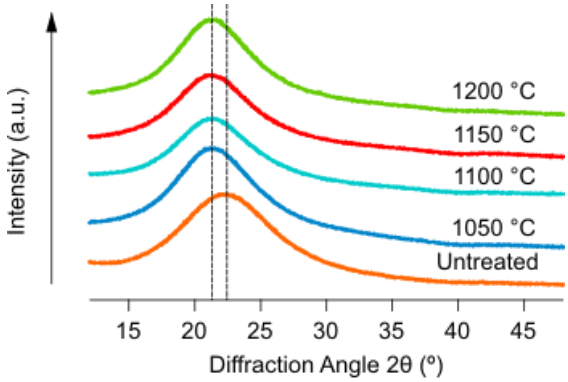

Figure S3. X-ray powder spectra of the heat-treated particles versus the diffraction angle. The intensity is given in arbitrary units (a.u.) and for clarity the spectra are shifted vertically. The dotted lines indicate the positions of the maxima for the untreated sample and the sample treated at 1200°C.

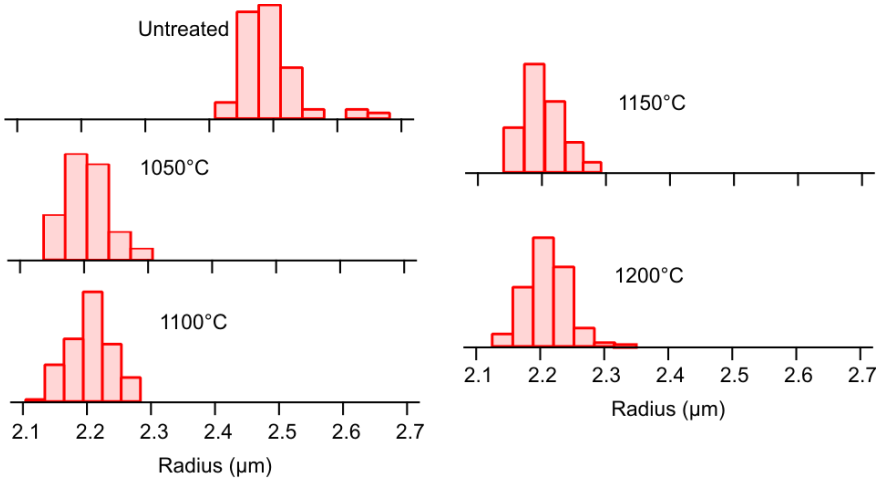

Figure S4. Number weighted size distributions obtained from SEM images. The resulting mean radius and coefficient of variation are summarized in Table S2.

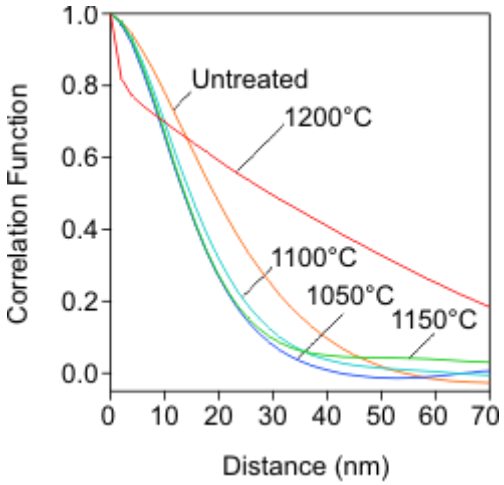

Figure S5. Radial height-height correlation function obtained from the AFM images for heat-treated particles at different temperatures.

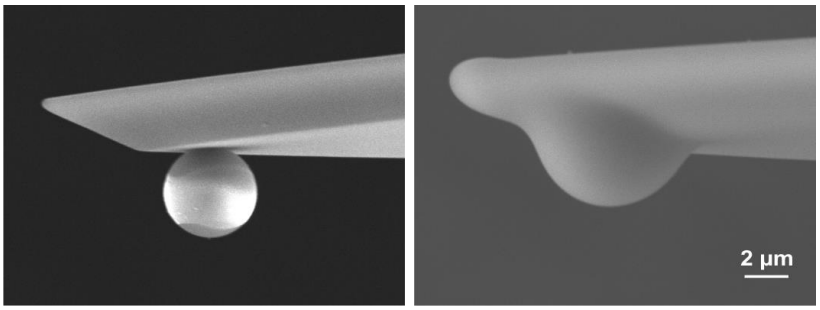

Figure S6. SEM image of the undeformed colloidal probe sintered at 1200°C (left) and of the deformed one that has melted at 1300° C (right). The deformed probes were not used for experiments.

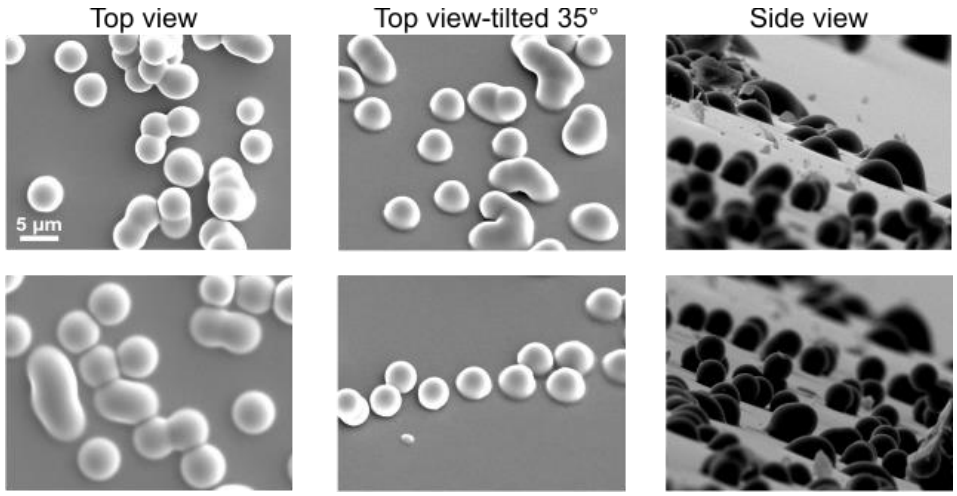

Figure S7. SEM images of the deformed particles deposited on the substrate when sintered at 1300°C. The deformed particles were not used for experiments.