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2 **Supporting Information for**

3 **Influence of Ionic Strength, pH, and Cation Valence on Aggregation Kinetics**

4 **of Titanium Dioxide Nanoparticles**

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29 **Summary of Contents**

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Materials and Methods

Preparation of nano-TiO₂ suspensions. The nano-TiO₂ sol-gel suspension was dialyzed using dialysis tubing (Spectra/Por 7 MWCO= 2000 Da) against DI water (Barnstead™ RO feed source, Barnstead™ Millipore MilliQ system, resistivity 18 MΩ-cm, with a Barnstead™ Millipore Super-Q Organex Q filter and a Durapore TP cartridge). A flow-through system attached to the DI water feed allowed for the water to be renewed constantly. The sealed dialysis tubes containing the sol-gel suspension were submerged in this system with stirring for three days. After synthesis was complete, a stock suspension of cleaned particles was stored, without further treatment, in an amber glass bottle in the dark at 4°C. Prior to experiments an aliquot of the original stock of nano-TiO₂ was diluted, placed in an ultrasonic bath for one hour, and filtered through a 0.45 µm cellulose filter to remove large artifact aggregates. The Ti concentrations of the resulting suspensions were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES) elemental analysis. Standards were prepared using 10,000 mg L⁻¹ titanium ICP standard (Ultra Scientific) in DI water. ICP-AES analyses were run in triplicate for each stock suspension prepared with a relative standard deviation of less than 2.4 %. The standard addition method was performed on one stock suspension and showed that recovery of Ti in spiked nano-TiO₂ suspensions ranged between 102 and 104 %.

Determining ionic strength. The ionic strength was calculated using the following equation:

$$I = \frac{1}{2} \sum_i c_i z_i^2$$

where ionic strength (I) equals the one half the sum of the concentration (c_i) times the charge squared (z_i^2) for each ion in solution. In the case of the suspensions of pH 6.8-8.2 the buffer was not incorporated into the calculation for ionic strength because HEPES is a buffer that was

1 especially developed to have low salt effects and low metal binding for studies on biological
2 systems, therefore it does not contribute greatly to ionic strength (1).

3 **Cryo-transmission electron microscopy (cryo-TEM).** The stable nano-TiO₂ aggregate
4 suspension from replicate 1 (see Figure S3) of 83 mg L⁻¹ TiO₂, 0.001 M NaCl, and pH 4.5 was
5 used for the cryo-TEM analysis without further treatment (see Materials and Methods main
6 document “Suspensions with different ionic strength and cation valence.”). A droplet of this
7 suspension was placed on a lacey carbon-coated grid and thinned by blotting. The sample was
8 vitrified in a “nitrogen slush” composed of dry ice and liquid nitrogen and transferred to a Gatan
9 model 626 Cryotransfer System. Cryo-TEM micrographs were taken on a Tecnai 12 Biotwin
10 transmission electron microscope. Images were collected using a Gatan model 791 multiscan
11 camera.

12 **X-Ray Diffraction.** Three specimens were prepared for X-ray analysis as previously described
13 by Isley and Penn (2). In brief, 400 µL aliquots of the nano-TiO₂ suspension were placed onto a
14 zero-background quartz slide and allowed to air-dry. Diffraction patterns were collected from 24-
15 62° (2θ) using a PANalytical X’Pert Pro diffractometer. The diffractometer was equipped with a
16 high speed X’Celerator detector and a Co Kα radiation source (45 kV, 40 mA). The method of
17 collection used the continuous scanning mode, with a step size of 0.016°, a dwell time of 765 s, a
18 0.5° divergent slit, and a 1° anti-scattering slit. Experimental patterns were compared to
19 International Centre for Diffraction Data’s powder diffraction files # 01-073-1764 for anatase, #
20 00-029-1360 for brookite, and # 01-072-1148 for rutile, respectively, for initial phase
21 composition determinations.

22 Quantitative phase composition was determined by the Rietveld refinement method (3),
23 which is a whole-pattern fitting method that uses a least-squares approach to systematically vary
24 constraints in a simulated theoretical line profile to match and minimize differences from that of

the experimental pattern. The refinements were performed using X'Pert High Score Plus (version 2.0.1) software and the known crystal structure data for anatase, brookite, and rutile as starting points (4). The parameters refined were zero shift ($^{\circ}2\theta$), background, scale factor, preferred orientation, the extinction coefficient, the W, U and V profile parameters, the unit cell parameters, and peak shapes. Goodness-of-fit (GOF, 1.6-2.7) and R weighted profile (Rwp, 1.5-2.0) values were monitored to ensure accurate fits between the observed and calculated data. The error reported in the phase percentage represents the standard deviation of three refinements. The Scherrer equation (5) was used to calculate average particle sizes from the full width at half maximum values of the anatase (101) and brookite (111, 120, and 121) peaks after correcting for instrumental broadening.

Electrophoretic mobility. An aliquot of the 120-128 mg L⁻¹ stock suspension of TiO₂ was adjusted to an ionic strength of 0.008 M with NaCl and to pH ~ 4.3 with 0.005 M HCl. A 100-mL subsample of the adjusted suspension was sonicated in an ultrasonic bath for 1 hour. After cooling the suspension for at least 3 hours, it was placed in a sealed container under N₂. The sample was then titrated with freshly prepared 0.008 M NaOH while stirring at 25 ± 1°C. Once the pH stabilized an aliquot was removed from the suspension and placed into the zeta potential cell. The electrophoretic mobility of the particles was measured using a Zetasizer Nano-ZS (Malvern Instruments). The temperature in the Zetasizer was set to 25 ± 0.1°C. Three replicate electrophoretic mobility measurements were made for each sample. The electrophoretic mobility values were converted to zeta potentials using the Smoluchowski approximation for the Henry equation. The pH of the suspension in the titration apparatus was measured before and after a zeta potential measurement was taken. The average of these two pH values was plotted versus the average of the three zeta potential values to determine the isoelectric point of the nano-TiO₂ suspension. The titrations and zetapotential measurements were performed in triplicate.

1 **Optical microscopy.** Images of the nano-TiO₂ were obtained by placing a few drops of a
2 suspension on a glass slide under an epoxy-sealed cover slip with spacers. This kept the sample
3 wet throughout the imaging process, thus reducing aggregation artifacts caused by drying. Images
4 were taken using a Hirox KH-7700 digital microscope with a MX-10C lens, OL-140 objective,
5 and coaxial illumination. All the images were collected within one week of the initial DLS
6 measurements of the suspensions.

Results and Discussion

Particle characterization.

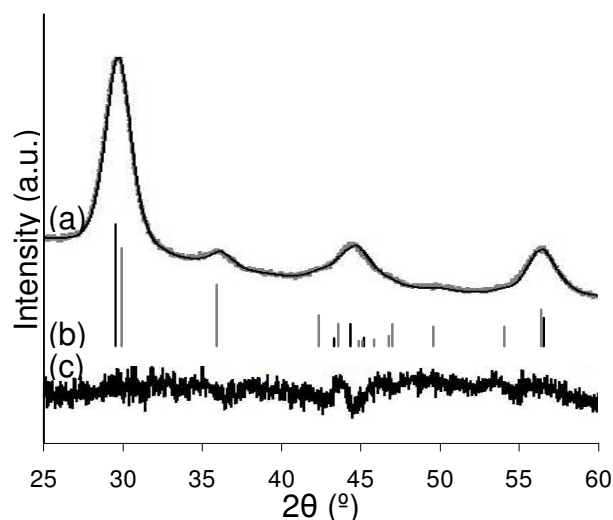


Figure S1. (a) Observed (■, gray) and calculated (—, black) XRD patterns, resulting from the Rietveld analysis of TiO_2 sample. (b) Lines correspond to PDF of anatase (#01-073-1764, black) and brookite (#00-029-1360, gray). (c) Difference profile between the observed experimental pattern and the calculated Rietveld pattern.

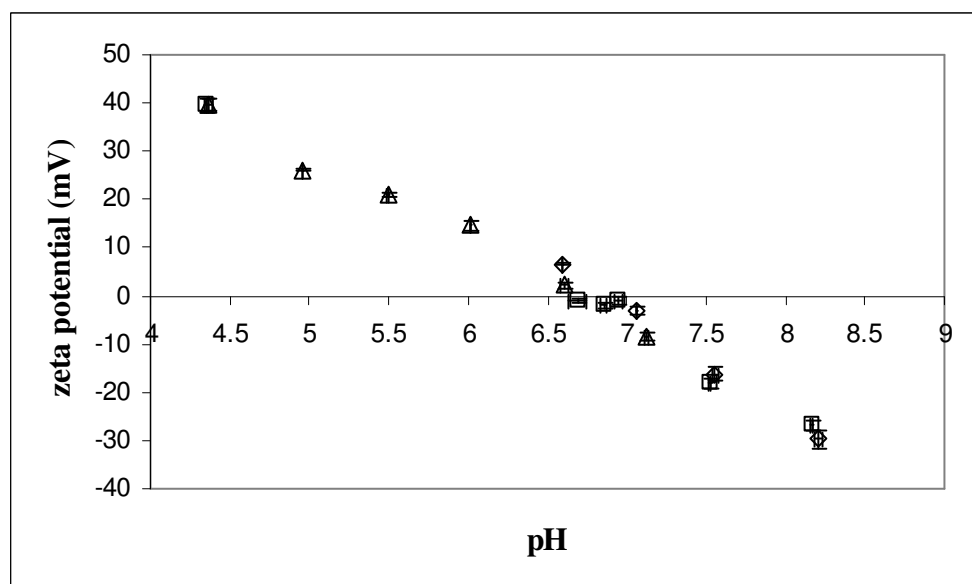
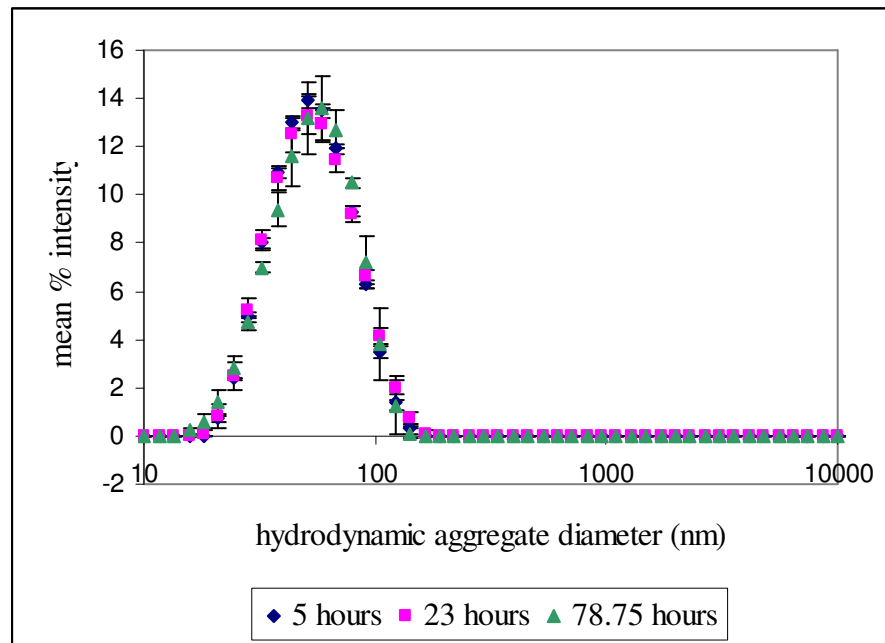
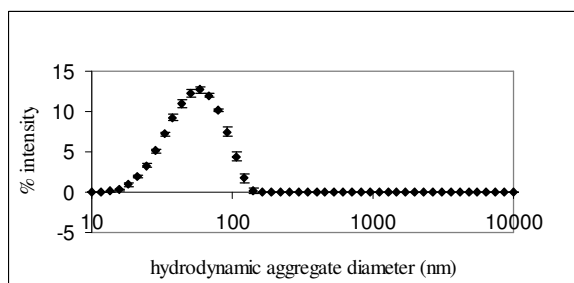


Figure S2. A plot of zeta potential versus pH for three replicate titrations on nano-TiO₂. The error bars represent the standard deviation of three subsequent measurements of zeta potential or the standard deviation of the pH measured before and after the zeta potential measurement.

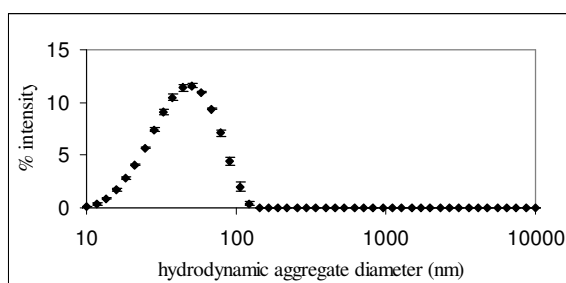
1 Initial aggregation of suspensions.



(a)



(b)



(c)

Figure S3. The average initial aggregate size (prior to increasing the salt concentration with NaCl solutions) measured for suspensions at 80 to 83 mg L⁻¹ TiO₂, 0.001 M ionic strength with a NaCl background electrolyte at pH ~4.5. (a) replicate 2 demonstrates the stability of the initial aggregate nano-TiO₂ suspension over time. Time zero starts at the end of the 1 hour sonication step (see Materials and Methods), i.e. the first DLS measurement was taken 5 hours after the suspension was sonicated, then 23 hours later and finally 78.75 hours later; Example size distributions for replicate studies: (b) replicate 3; (c) replicate 1. Error bars represent standard deviation of three measurements.

1 **Table S1.** The first 15 measurements of hydrodynamic radius were made over approximately 35
2 minutes. Although each measurement gives a broad distribution of particle sizes the mean of
3 these distributions has been used to determine numerical rates of aggregation in previous studies
4 (5,6). In the case of the ionic strength of 0.0125 and 0.0085 M NaCl and pH ~4.5 the data was
5 linear. In the case of 0.0165 M NaCl and pH ~4.5 the data was only linear through the first 3 to 5
6 data points after which our suspensions became very polydisperse. The initial aggregation rate
7 was determined by fitting a linear regression to these initial data points and then calculating its
8 first derivative. This table summarizes the data. The mean initial aggregation rate clearly shows
9 that as ionic strength increases so does the initial rate of aggregation. The % relative standard
10 deviation (% RSD) is large, but this is not unexpected considering that these values were based
11 on suspensions with a wide distribution of particle sizes and that only two initial rates were used
12 to calculate the mean at each ionic strength.

Sample	Mean Linear Regressions R^2	Mean Initial Aggregation Rate (nm/min)	Standard Deviation (nm/min)	% RSD
0.0085 M NaCl	0.959	1.127	0.3262	28.93
0.0125 M NaCl	0.986	5.863	1.788	30.50
0.0165 M NaCl	0.987	86.78	35.27	40.64

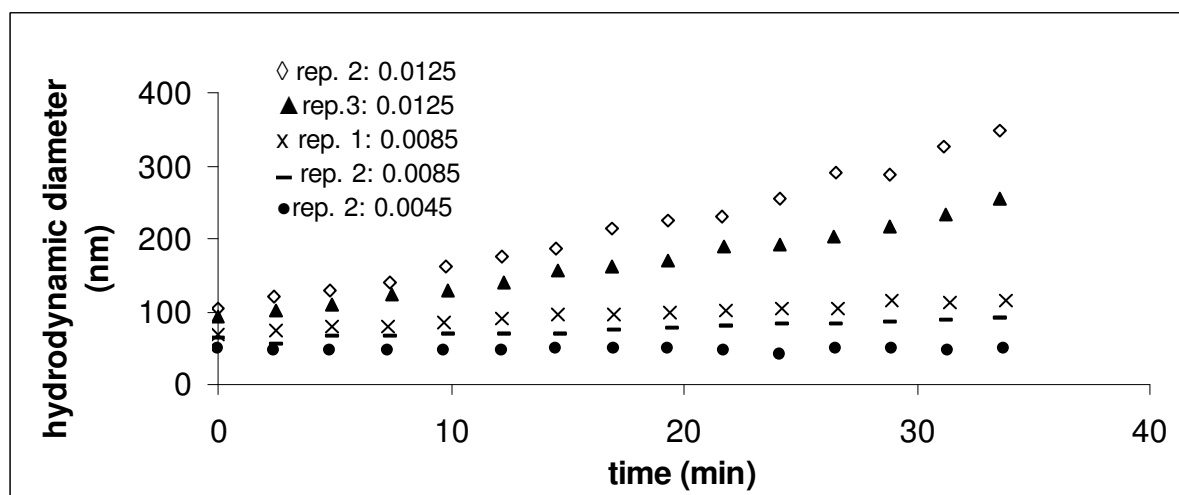


Figure S4. These data are the mean hydrodynamic diameters for the first 15 data points measured every 2 minutes over the first 35 minutes of the experiment for the suspensions at pH ~4.5 with ionic strengths from 0.0045 M to 0.0125 M NaCl. These means represent at least 99.5% of the total intensity-weighted peak area aggregate size distribution.

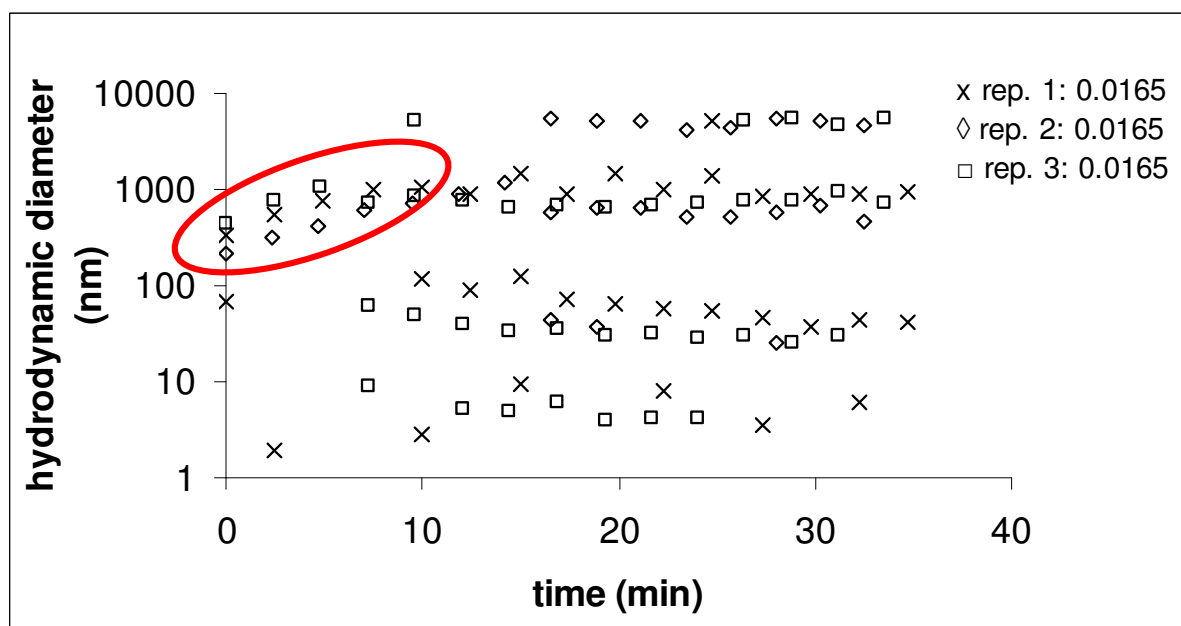


Figure S5. This figure shows the replicate data for the pH ~4.5 and 0.0165 M NaCl samples. These suspensions are polydisperse as indicated by the multiple mean values for the particle size distributions at each measurement. Data used for the linear regression in Table S1 is circled in red. The replicate 1 (rep. 1) data (x) from 0 to 10 minutes that were not used in the linear regression calculation represent less than 15% of the total peak area. The first three data points of replicate 3 (rep. 3) were the only points used for the linear regression in this case. Note that the values represented above are all mean size values, but they are not weighted by their intensity as in Figure 3b (see main document). Also note that this figure does not fully describe which aggregate sizes dominate the suspension at any time, i.e. not all of the means carry equal weight.

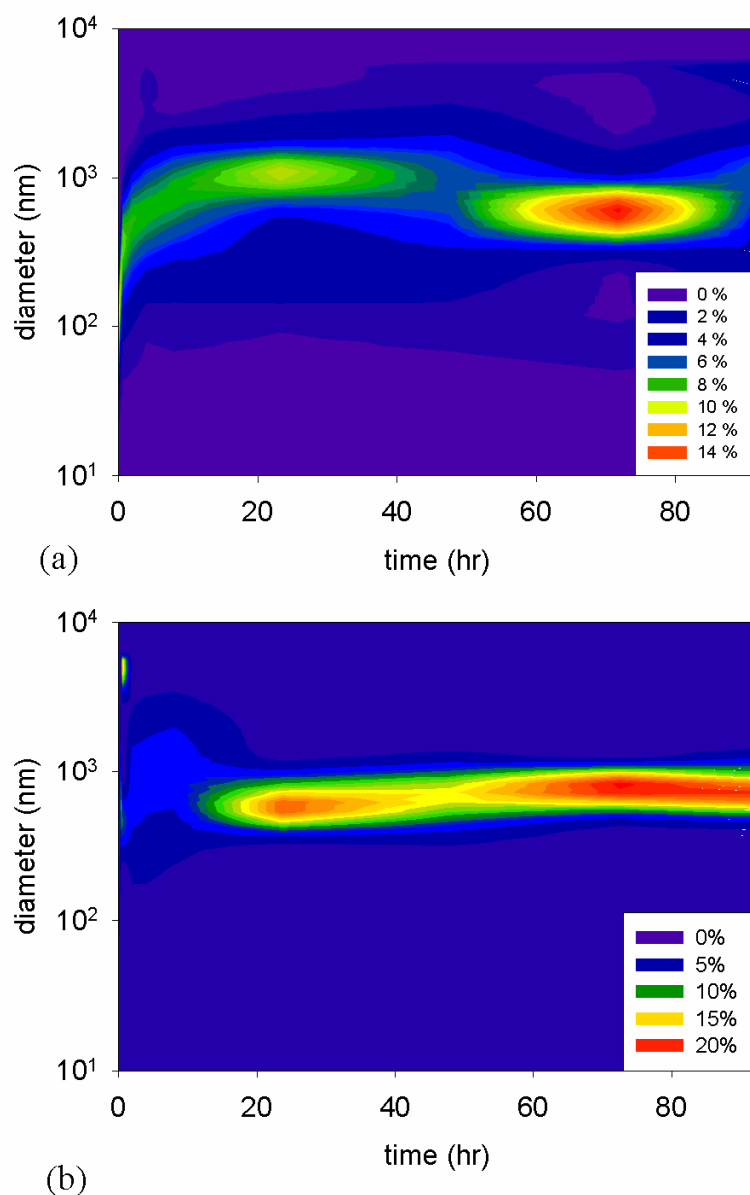


Figure S6. Aggregation of nano-TiO₂ measured over 5 days. The suspension contained 40 to 42 mg L⁻¹ nano-TiO₂ at pH 4.5. The ionic strength was adjusted with NaCl. The colors represent the intensity of light (%) scattered by aggregates in suspension. (a) 0.0125 M NaCl ; (b) 0.0165 M NaCl.

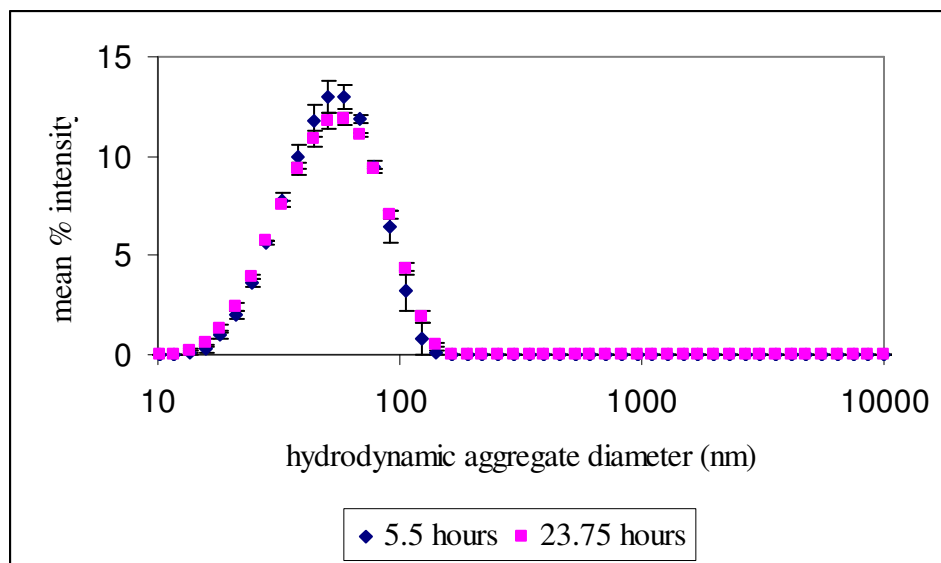


Figure S7. Starting aggregate size (prior to increasing salt concentration with CaCl_2) for cation valency experiments with 80 mg L^{-1} nano- TiO_2 in 0.001 M CaCl_2 at pH 4.8. The two data sets demonstrate the stability of the initial aggregate nano- TiO_2 suspension over time. Time zero starts at the end of the 1 hour sonication step, i.e. the first DLS measurement was taken 5.5 hours after the suspension was sonicated (see Materials and Methods). Error bars represent standard deviation of three measurements.

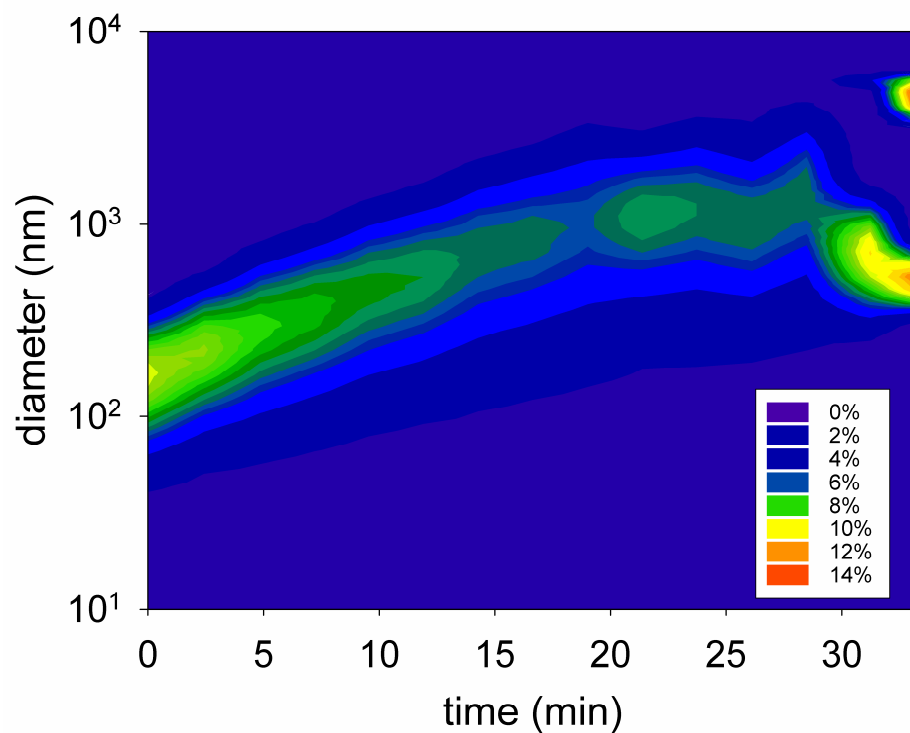
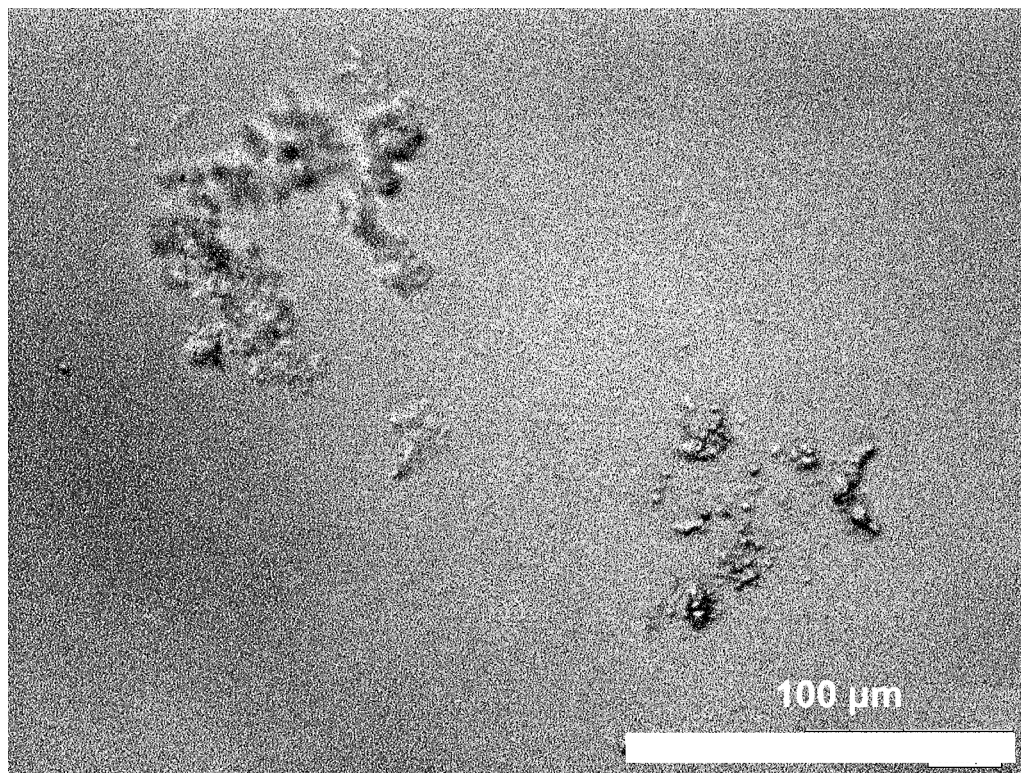


Figure S8. Replicate aggregation kinetics measurement for ionic strength 0.0128 adjusted with CaCl_2 and pH 4.8. Colors represent an intensity-weighted particle size distribution.

1 **Aggregation of nano-TiO₂ under pH and ionic strength ranges typical of soils.**

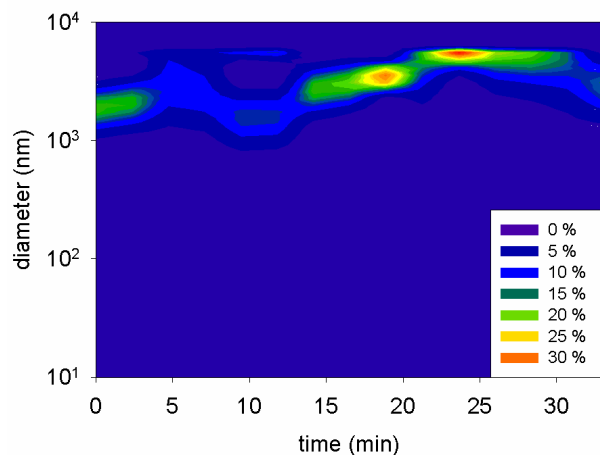
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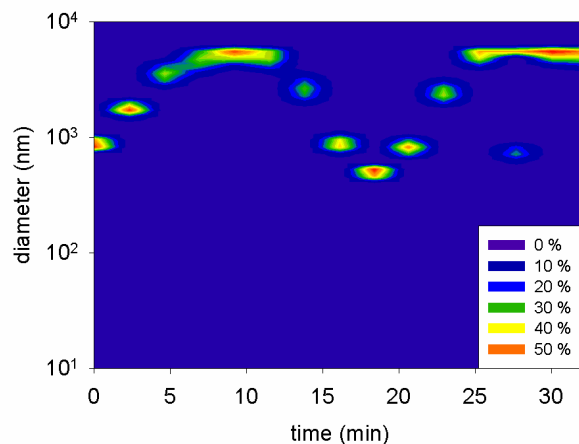
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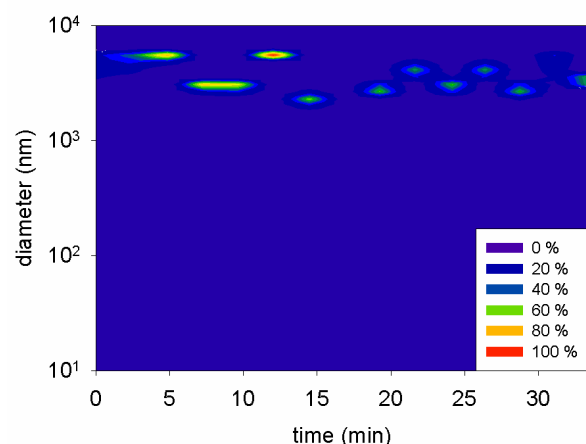
5 **Figure S9.** Optical image of nano-TiO₂ aggregates in a pH 7.5 aqueous suspension adjusted to an
6 ionic strength of 0.0093 M with NaCl.



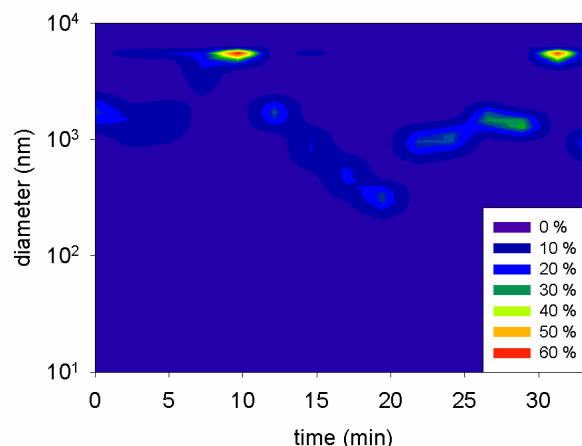
(a)



(b)

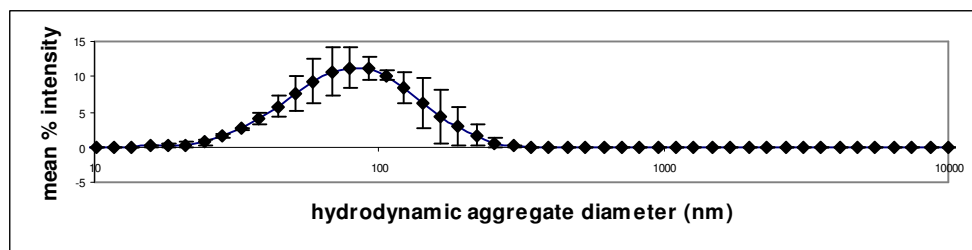


(c)

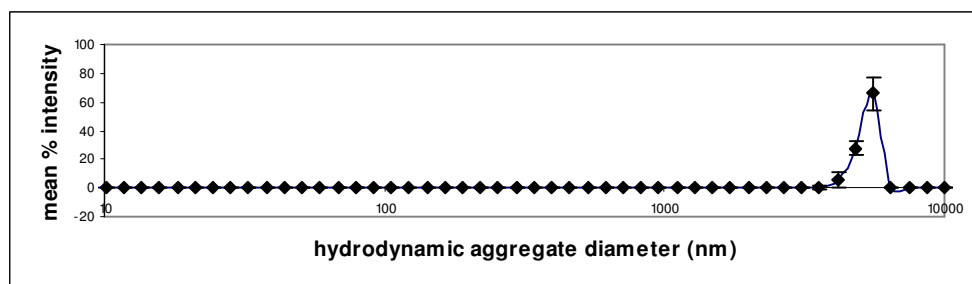


(d)

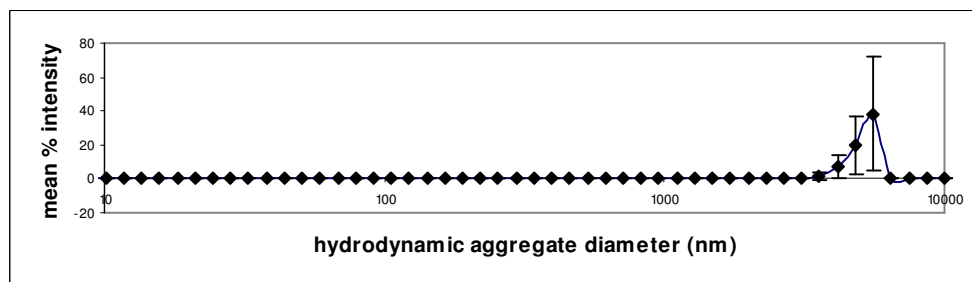
Figure S10. Representative aggregation of 42 mg L⁻¹ nano-TiO₂ over 35 minutes in suspensions of different pH and ionic strength. (a) pH 5.8 and ionic strength 0.0085 M; (b) pH 6.8 and ionic strength 0.0084 M; (c) pH 7.5 and ionic strength 0.0093 M; (d) pH 8.2 and ionic strength 0.0099. All aggregation studies for pH 5.8 to pH 8.2 were performed in duplicate. Similar aggregation patterns were observed in duplicate studies. The colors represent the intensity of light (%) scattered by aggregates in suspension.



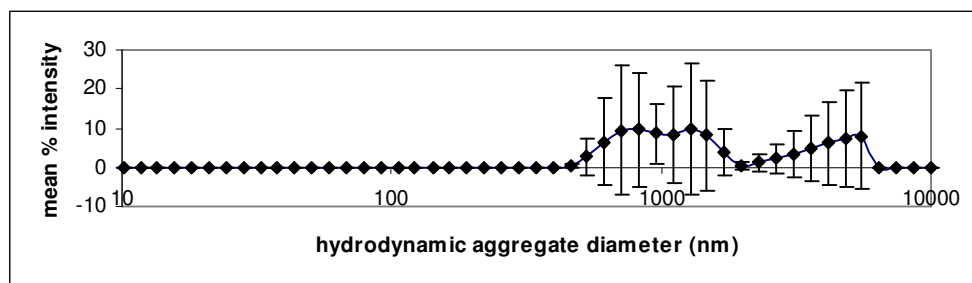
(a)



(b)

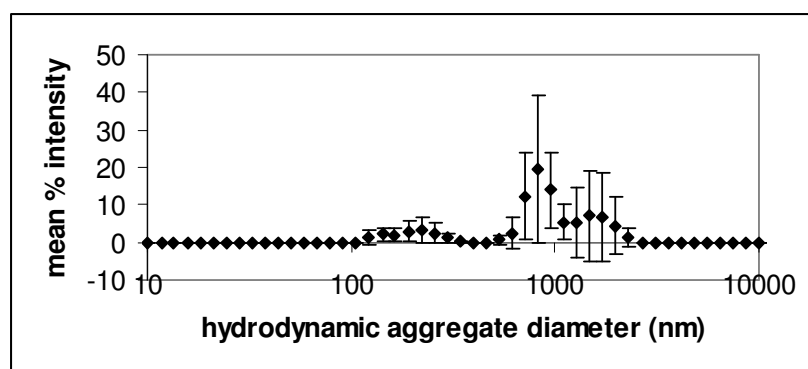


(c)

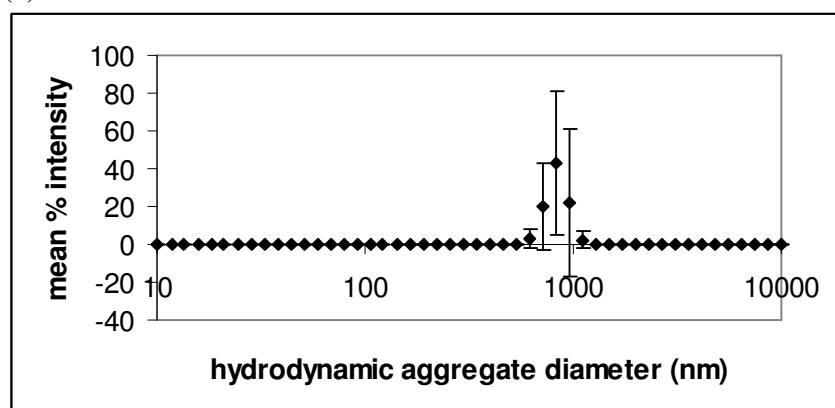


(d)

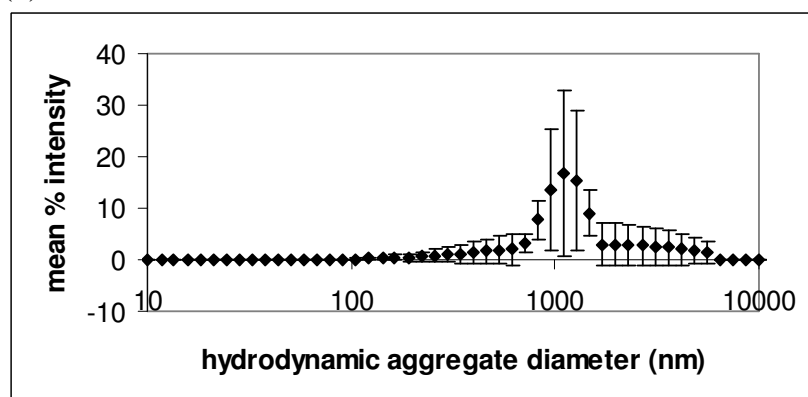
Figure S11. Initial aggregate size (prior to increasing salt concentration with NaCl) for variable pH experiments. Error bars represent the standard deviation of three measurements. All suspensions contained 83 mg L^{-1} nano-TiO₂. The pH of the suspensions were adjusted with NaOH. If necessary, the ionic strength of the suspensions was further adjusted with NaCl. (a) pH 5.8 and 0.001 M NaCl; (b) pH 6.8 and 0.0013 M NaOH; (c) pH 7.5 and 0.0045 M NaOH; (d) pH 8.2 and 0.0081 M NaOH. The error bars include zero in some cases because of the large standard deviations associated with the three consecutive measurements.



(a)

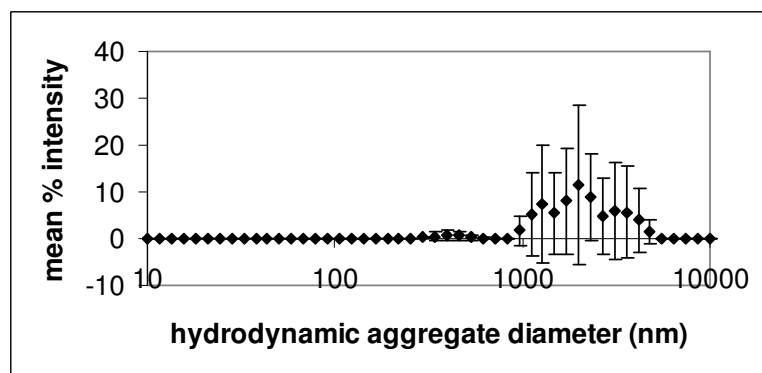


(b)

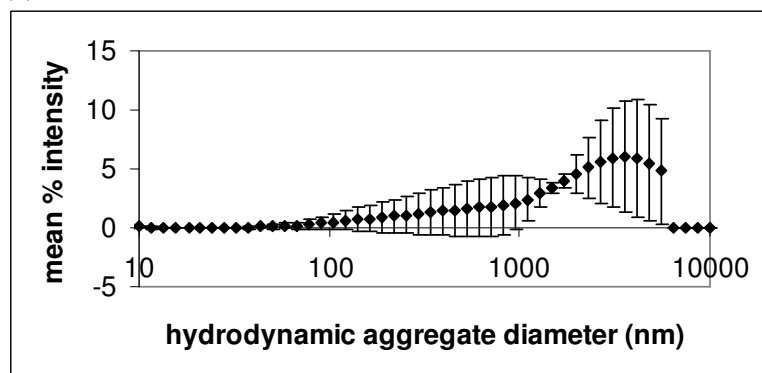


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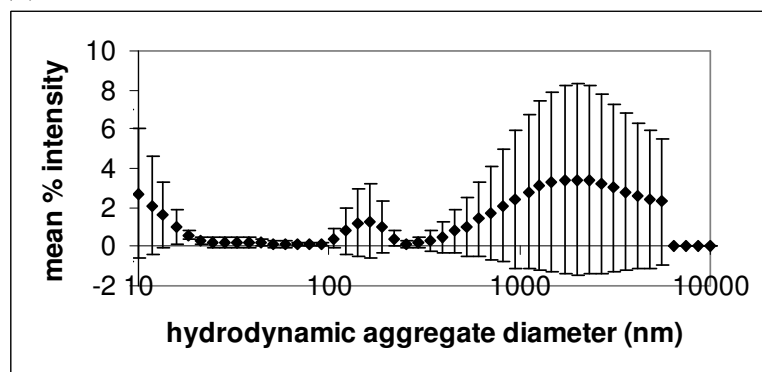
Figure S12. Aggregates remaining in suspension after allowing the aggregates to settle undisturbed for two weeks. Error bars represent the standard deviation of three consecutive measurements per sample for (a) and (b). Error bars in (c) represent the standard deviation of duplicate measurements because the results of one replicate were below detection. (a) pH 8.2, sample 1; (b) pH 8.2, sample 2; (c) pH 5.8, sample 1. The error bars include zero in some cases because of the large standard deviations associated with the three consecutive measurements.



(a)



(b)



(c)

Figure S13. Aggregates remaining in suspension after allowing the aggregates to settle undisturbed, for two weeks. Error bars represent the standard deviation of three consecutive measurements per sample for (a) and (b). Error bars in (c) represent the standard deviation of duplicate measurements because the results of one replicate were below detection. (a) pH 7.5, sample 1; (b) pH 7.5, sample 2; (c) pH 6.8, sample 1. The error bars include zero in some cases because of the large standard deviations associated with the three consecutive measurements.

Literature Cited

1. Good, N. E.; Winget, G. D.; Winter, W.; Connolly, T. N.; Izawa, S.; Singh, R. M. M.,
Hydrogen Ion Buffers for Biological Research. *Biochemistry* **1966**, 5 (2), 467-477.
2. Isley, S. L.; Penn, R. L. *J. Phys. Chem. B* **2006**, 110, 15134
3. Rietveld, H. M. *J. Appl. Crystallogr.* **1969**, 2, 65.
4. Wyckoff, R. W. G. *Crystal Structures. Vol. 1. 2nd ed*, 1963.
5. Scherrer, P. *Göttinger Nachrichten* **1918**, 2, 98.