

Supplementary Information

Aggregation of Chemical Mechanical Planarization Nanoparticles and their Interactions with Model Biological Membranes: Role of Phosphate Adsorption

XITONG LIU and KAI LOON CHEN*

Department of Geography and Environmental Engineering, Johns Hopkins University, Baltimore, Maryland 21218-2686
(*E-mail: kailoon.chen@jhu.edu)

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References.

Additional Details on Materials and Methods

Cleaning of CMP NPs for Phosphate Adsorption Experiments

The CMP NPs in the stock suspensions were washed before being used for the phosphate adsorption experiments. For the *f*-SiO₂, CeO₂, and Al₂O₃ NPs, 50 mL of each NP suspension was centrifuged at 3,650 g (Beckman Coulter, CA, 4,000 rpm) for 3 h. 90 % of the supernatant was carefully decanted and replaced with an equal volume of deionized (DI) water. This cleaning process was repeated two times. For the *c*-SiO₂ NPs, a similar procedure was used, except that the centrifugation was performed at 12,000 g (Eppendorf, NY, 13,375 rpm) for 40 min and the cleaning process was repeated four times. The concentrations of the *c*-SiO₂, *f*-SiO₂, CeO₂, and Al₂O₃ NPs in the washed suspensions were determined to be 22.5 ± 1.3 , 46.3 ± 7.8 , 5.5 ± 0.1 , and 19.4 ± 0.3 g/L, respectively, by gravimetric analysis.

Phosphate Adsorption Experiments

Adsorption experiments were conducted in glass scintillation vials at room temperature. These experiments were conducted at an initial phosphate concentration of 100 μ M, 1 g/L NPs, 1 mM NaCl, and pH 7.4. Two duplicate adsorption reactors were set up for each type of NPs. After the suspension was stirred on a magnetic stir plate at 400 rpm for 10 min, aliquots of the suspension were drawn and centrifuged at 12,000 g (Eppendorf, NY, 13,375 rpm) for 40 min. The concentration of phosphate in the supernatant was determined using the colorimetric technique of Murphy and Riley.¹ Briefly, 0.06 mL of 11 N H₂SO₄ was added to 3 mL of the supernatant, followed by the addition of 0.24 mL of 8 g/L ammonium molybdate (Fluka) and 0.2 g/L antimony potassium tartrate (Sigma-Aldrich). The resulting solution was mixed to allow for the formation of an antimony-phospho-molybdate complex. Next, 0.12 mL of 60 g/L ascorbic acid (Sigma-Aldrich) was added to the solution to reduce the complex to a blue-colored complex. The absorbance of the solution was measured with a UV/Vis spectrophotometer (Shimadzu, UV-1800) at 650 nm. A linear calibration curve was obtained over the range of phosphate concentration of 0–25 μ M.

Control experiments were also performed on the four CMP suspensions without the addition of phosphate. Two duplicate control reactors were set up for each NP. Each control reactor contains 1 g/L CMP NPs and 1 mM NaCl. After 10 min of stirring, aliquots of the control suspensions were drawn, centrifuged, and measured in a similar manner as the NP-

phosphate suspensions (described in the previous paragraph). The absorbance of the supernatants of the control suspensions at 650 nm was subtracted from that of the supernatants of the NP-phosphate suspensions. The concentrations of phosphate in the supernatants of NP-phosphate suspensions were determined using the calibration curve and the amount of phosphate adsorbed on the NPs was calculated through material balance (expressed as $\mu\text{mol phosphate/g NPs}$).

Dynamic Light Scattering

Time-resolved dynamic light scattering (DLS) measurements were conducted with a light scattering unit to investigate the aggregation kinetics of four CMP NPs in phosphate and bicarbonate buffers. This unit consists of an argon laser with a wavelength of 488 nm (Lexel 95, Cambridge laser, CA), a photomultiplier tube mounted on a goniometer (BI-200SM, Brookhaven, NY), a digital correlator (BI-9000AT, Brookhaven, NY), and a thermostatted vat filled with an index-matching *cis*- and *trans*-mixture of decahydronaphthalene. The room temperature was maintained at 25 °C. New glass vials were soaked overnight in a cleaning solution (Extran MA01, Merck KGaA, Darmstadt, Germany), rinsed thoroughly with DI water, and dried in an oven under dust-free conditions prior to use. For each aggregation experiment, a predetermined amount of NaCl solution was introduced to a glass vial containing a diluted suspension of CMP NPs. The pH of the suspension was maintained at 7.4 with either phosphate or bicarbonate buffer, or adjusted to 1.0, 2.0, and 12.0 using 1 M HCl or NaOH. The total volume of the suspension was 1 mL. The suspension in the vial was briefly mixed using a vortex mixer. The vial was then inserted into the index-matching vat and the DLS measurements were started immediately. All DLS measurements were performed at a scattering angle of 90° and each autocorrelation function was accumulated for 15 s. The intensity-weighted hydrodynamic diameters of the aggregates were derived through second-order cumulant analysis (Brookhaven software). The DLS measurements were performed over time periods of 10–50 min to allow for a large enough increase in the intensity-weighted hydrodynamic diameter for an accurate determination of the NP aggregation kinetics.

TABLE S1. Concentrations of CMP NPs used in electrophoretic mobility measurements.

Name	<i>c</i> -SiO ₂	<i>f</i> -SiO ₂	CeO ₂	Al ₂ O ₃
Dilution factor	100	1,000	1,000	1,000
Concentration	270 mg Si L ⁻¹	50 mg Si L ⁻¹	9.6 mg Ce L ⁻¹	29 mg Al L ⁻¹

TABLE S2. Concentrations of CMP NPs used in dynamic light scattering measurements.

Name	<i>c</i> -SiO ₂	<i>f</i> -SiO ₂	CeO ₂	Al ₂ O ₃
Dilution factor	1,000	25,000	5,000	25,000
Concentration	27 mg Si L ⁻¹	2 mg Si L ⁻¹	1.92 mg Ce L ⁻¹	1.16 mg Al L ⁻¹

TABLE S3. Concentrations of CMP NPs used in quartz crystal microbalance experiments.

Name	<i>c</i> -SiO ₂	<i>f</i> -SiO ₂	CeO ₂	Al ₂ O ₃
Dilution factor	10,000	25,000	1,000	10,000
Concentration	2.7 mg Si L ⁻¹	2 mg Si L ⁻¹	9.6 mg Ce L ⁻¹	2.9 mg Al L ⁻¹

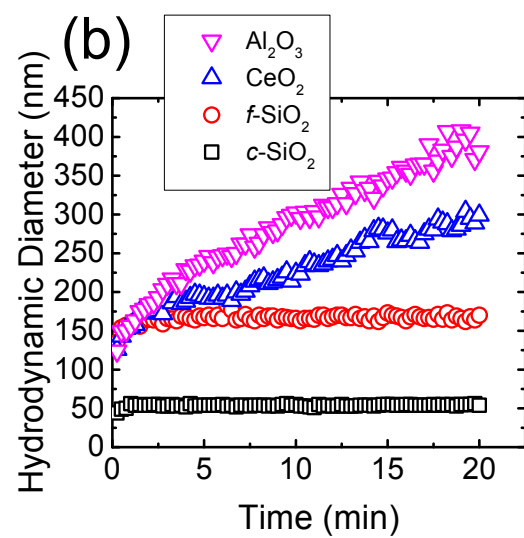
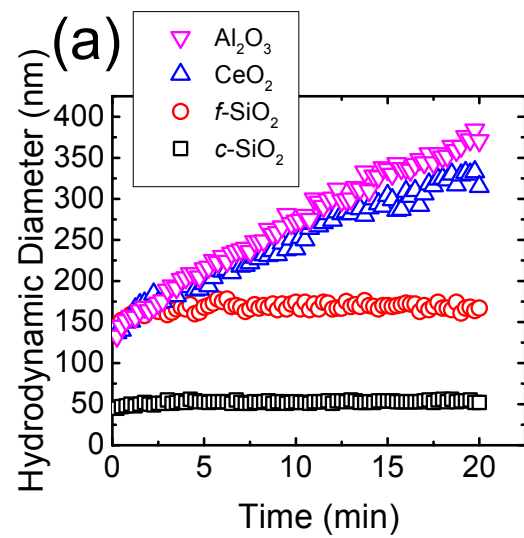


FIGURE S1. Aggregation profiles of four CMP NPs at 150 mM NaCl and pH 7.4 in (a) phosphate and (b) bicarbonate buffer.

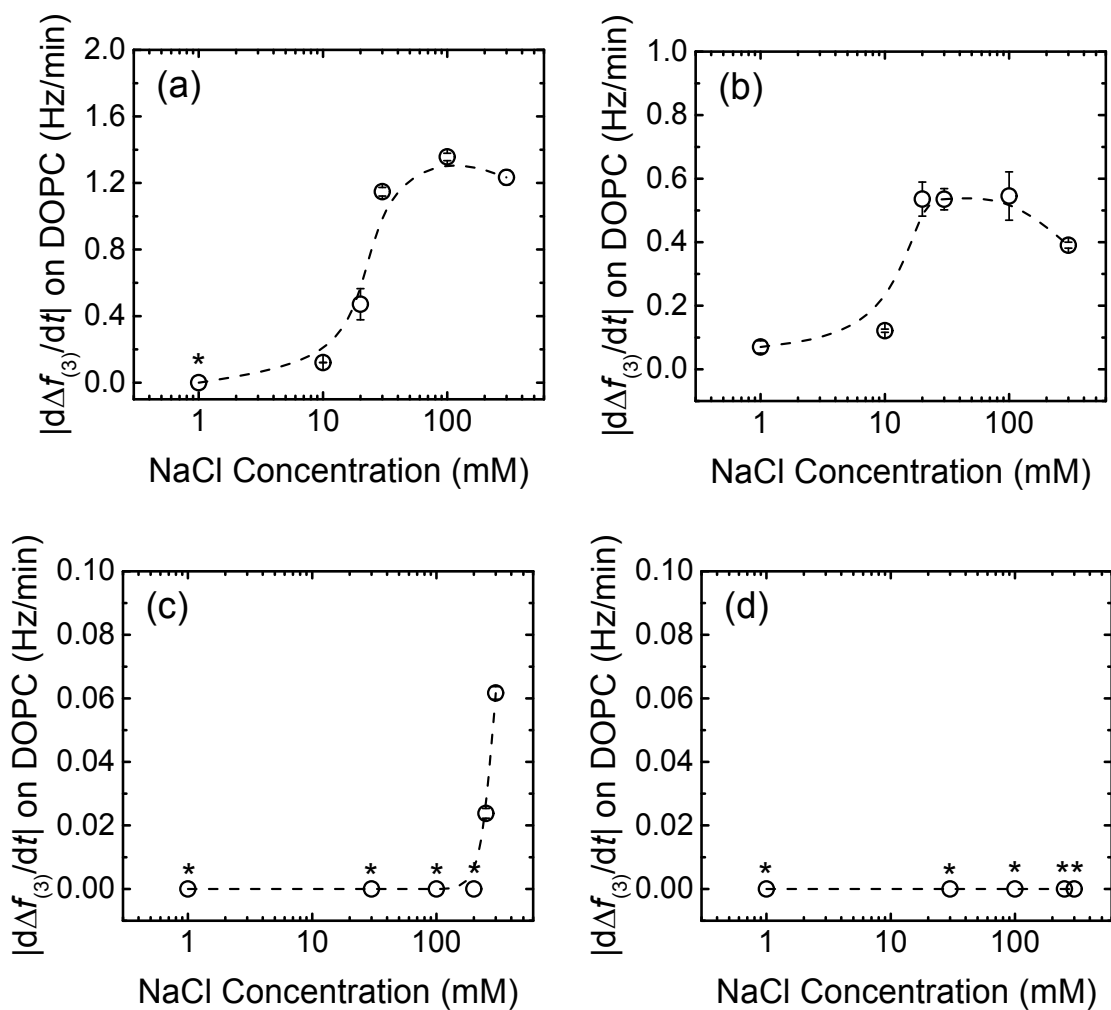


FIGURE S2. Deposition rates of (a) *c*-SiO₂, (b) *f*-SiO₂, (c) CeO₂, and (d) Al₂O₃ NPs on DOPC SLBs in phosphate buffer at pH 7.4. Error bars represent standard deviations and the lines are meant to guide the eye. Asterisks (*) indicates that no frequency shift was detected.

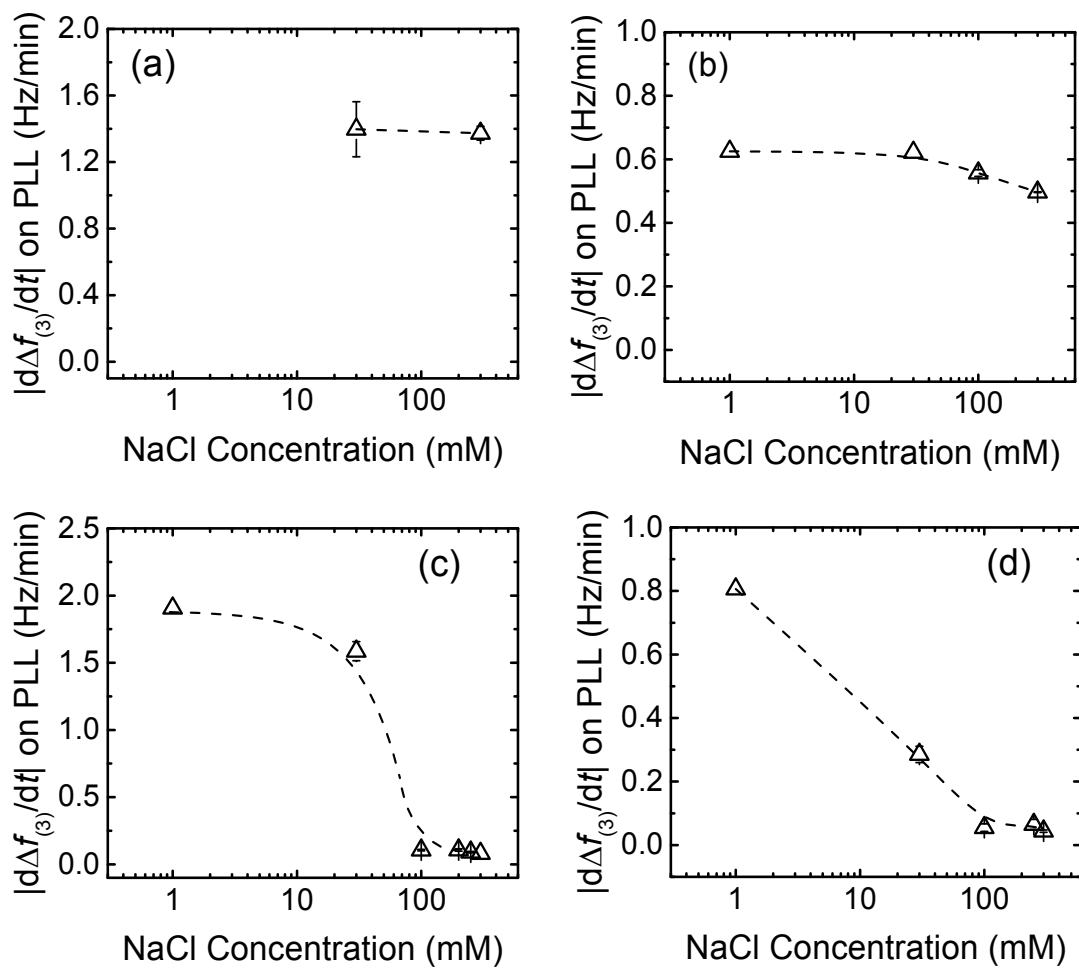


FIGURE S3. Deposition rates of (a) $c\text{-SiO}_2$, (b) $f\text{-SiO}_2$, (c) CeO_2 , and (d) Al_2O_3 NPs on PLL-modified surfaces in phosphate buffer at pH 7.4. Error bars represent standard deviations and the lines are meant to guide the eye.

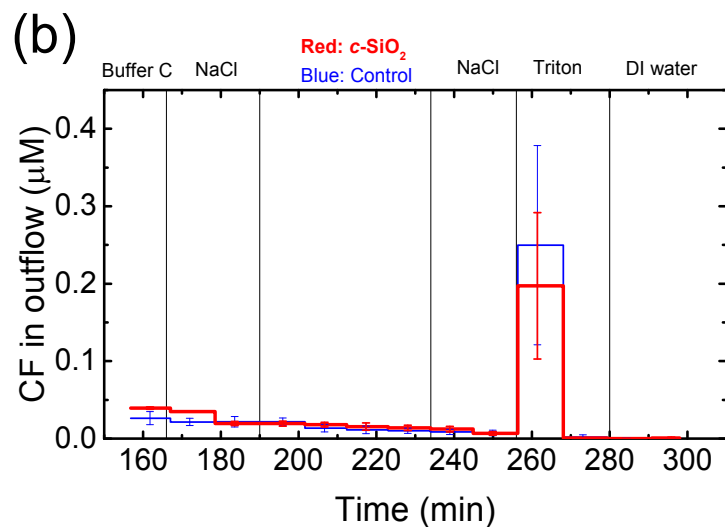
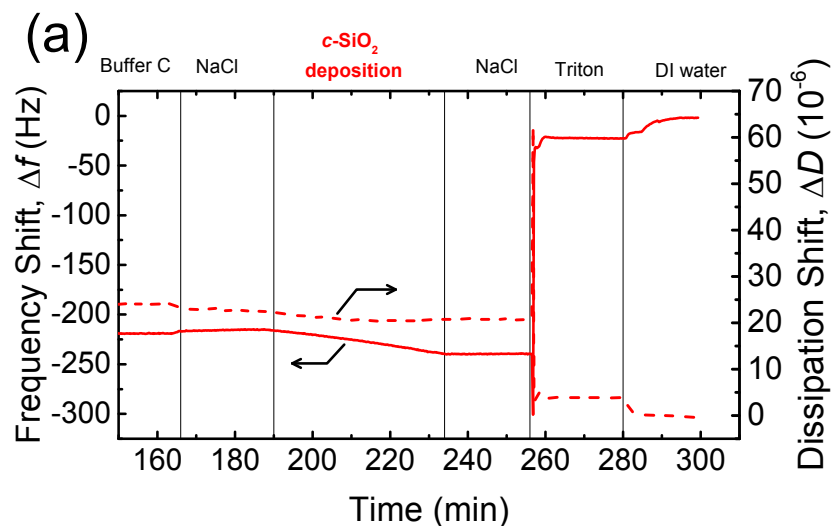


FIGURE S4. (a) Frequency and dissipation shifts when supported vesicles were exposed to *c*-SiO₂ NP suspension prepared at 150 mM NaCl (191–234 min), 150 mM NaCl solution (234–256 min), and 32 mM Triton X-100 solution (256–280 min). The solid and dash lines show the frequency and dissipation shifts, respectively. (b) Release of CF dye from supported vesicles when the vesicles were exposed to *c*-SiO₂ NP suspension prepared at 150 mM NaCl, 150 mM NaCl solution, and 32 mM Triton X-100 solution. The red and blue lines show the dye release profiles in the NP deposition and control experiments, respectively. Error bars represent standard deviations.

References

1. Murphy, J.; Riley, J. P., A modified single solution method for the determination of phosphate in natural waters. *Anal Chim Acta* **1962**, *27*, 31-36.