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Impacts of Particle Surface Heterogeneity on the Deposition of Colloids on Flat Surfaces

Supporting Information

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Preparation

Silicon (IV) Oxide nanoparticles (SiO_2 NPs) in powder form with an average particle size of 500 nm (99.9%) and density of 2.0 g/cm^3 was purchased from Alfa Aesar (Massachusetts, USA). Polymethyl methacrylate (PMMA), poly-L-lysine hydrobromide (PLL) with a molecular weight of 70,000 – 150,000 by viscosity, 3-aminopropyl triethoxysilane (APTES), and a cellulose membrane syringe filter with a pore size of 0.2 μm were purchased from Sigma Aldrich (St. Louis, USA). Silicon wafers (diameter of 50.8 mm, 0-100 ohm-cm, 320-350 μm thick) were purchased from University Wafer (USA).

The surface of SiO_2 NPs was cleaned with a piranha solution (a mixture of H_2SO_4 and H_2O_2) and rinsed with nanopure water (18.2 MΩ-cm, Barnstead Nanopure system). SiO_2 NPs were dried at 80°C in an oven overnight and dispersed in a 1% wt/wt solution of 4:1 deionized (DI) water:ethanol in an ultrasonic water bath (FS 60, 100 W, 42 kHz, Fisher Scientific, Pittsburg, PA). A 10% w/v PMMA solution was prepared by dissolving PMMA powder in toluene. The solution was sonicated and then submerged in a water bath at 80°C overnight. A 0.1 mg/mL PLL solution was prepared by dissolving PLL in DI water via sonication and subsequent filtering through a 0.2 μm syringe. Excess PLL was stored at 4°C.

pH was measured using Symphony B10P benchtop pH meter (VWR, Illinois, USA) and calibrated with pH calibration buffer (Hanna instruments, Rhode Islands, USA) before each batch of measurements. The pH was adjusted with 100 mM NaOH and 1 M HCl to reach desired pH. Specific surface area calculated based on particle size distribution data, and other physical parameters such as material density from equation below:

$$S_e = \frac{6\sum \frac{V_i}{d_i}}{\rho \sum V_i} = \frac{6}{\rho D_s}$$

Where Vi, relative volume by particle size class di; ρ, material density, and Ds, mean diameter based on surface area. In figure 3A, we showed that the mean particle size of control SiO2 is 712.4 nm. With the given density of SiO2, specific surface area, Se of SiO2 is calculated to be 4.21 m2/g.

Quartz Crystal Microbalance with Dissipation (QCM-D) experiments

Au-coated 5 MHz AT-cut quartz crystal sensors (QSX 301) were purchased from Biolin Scientific AB (Stockholm, Sweden). The sensor was cleaned with O_2 plasma for 20 minutes. To create surfaces with different surface properties, we deposited 4 nm aluminum oxide (Al_2O_3) or silica dioxide (SiO_2) films on sensor surfaces using atomic layer deposition (ALD) instrumentation (Fiji 200, Veeco Cambridge Nanotech)[38].

The SiO_2 ALD process employs the $C_6H_{18}N_3Si$ (tris(dimethylamino) silane, TDMAS) as the main precursor. The substrate temperature was maintained at 250°C, and 100 sccm argon as a carrier gas was continuously sent into the reactor chamber. Sixty ALD cycles led to a 4 nm layer of SiO2 on the QCM-D sensor surface. The Al_2O_3 ALD process employs an $Al(CH_3)_3$ trimethyl-aluminum (TMA, Strem 98%) as the main precursor. The substrate temperature was maintained at 150°C, and 200 sccm argon as a carrier gas was continuously sent into the reactor chamber. Forty-five ALD cycles led to a 4 nm layer of Al_2O_3 on the QCM-D sensor surface.

The sensors were cleaned with oxygen plasma on the same day as the Janus particle deposition experiment and were then mounted within the QCM-D chamber before the

experiment. A 1 mM NaCl solution with an adjusted pH of 7 ± 0.1 was introduced into the liquid cell at a flow rate of 0.1 mL/min. After frequency and dissipation changes achieved a baseline with a drift less than 0.25 Hz/hr for all reported overtones, 10 ppm of suspension containing Janus SiO_2 NPs, control SiO_2 NPs, or PLL- SiO_2 NPs in 1 mM NaCl with an adjusted pH of 7 ± 0.1 was flowed into the QCM-D liquid cell.

QCM-D measures shifts in resonance frequency and its odd-numbered harmonic overtones Δf_n, which indicate attachment or detachment of material to the surface. For QCM-D measurements, the alternating voltage is periodically turned off, allowing the oscillation amplitude to decay [39]. The dissipation parameter D_n is the time-dependent amplitude loss behavior of the resonance frequency and its harmonic overtones. Dissipation shifts (ΔD_n) indicate changes in surface viscoelasticity, as softer or ambient-swollen layers tend to dampen the decaying oscillation faster. [40] A thin film is considered rigid when the measured $\Delta f_n/n$ is independent of overtone order and if ΔD_n is very small relative to $\Delta f_n/n$, where $\Delta D_n/(-\Delta f_n/n) < 5 \times 10^{-8}$ Hz^{-1}. The viscoelastic properties of the film are considered when Δf_n spreads between different orders and a significant ΔD_n is recorded [41,42]. The Voigt-Kelvin-based model [43], which relates Δf_n and ΔD_n to areal mass density $m_{fQCM\text{-}D}$ and film viscoelastic properties, is typically used to analyze data for soft but laterally homogeneous films. Under simplified conditions, when $k_f d_f$ <<1, (k_f is the acoustic wavenumber, d_f is the film thickness), the viscoelastic model can be expressed as follows [40,44]:

$$\frac{\Delta f_n}{n} = -\frac{1}{C} m_{fQCM_D}\left(1 - n w_f \rho_l \eta_l \frac{G"}{\rho_f\left(G'^2 + G"^2\right)}\right), \quad (1)$$

$$\Delta D_n = 2\frac{1}{fC} m_{fQCM_D} n w_f \rho_l \eta_l \frac{G'}{\rho_f\left(G'^2 + G"^2\right)}, \quad (2)$$

where C is the mass sensitivity constant $(C = \sqrt{\rho_q \mu_q}/2f_f^2)$, $w_f = 2\pi f_f$ is the angular fundamental response frequency, and η_l and ρ_l are the viscosity and density of liquid, respectively. G = G' + iG" is the complex shear modulus parameter of the adsorbate. G' is the storage modulus parameter, which is related to material elasticity, and $G" = 2\pi n f_f \eta$, which is the loss modulus parameter, describes viscous energy dissipation in the material. The areal mass density was calculated by using recorded overtone numbers (n =3, 5, 7, and 9).

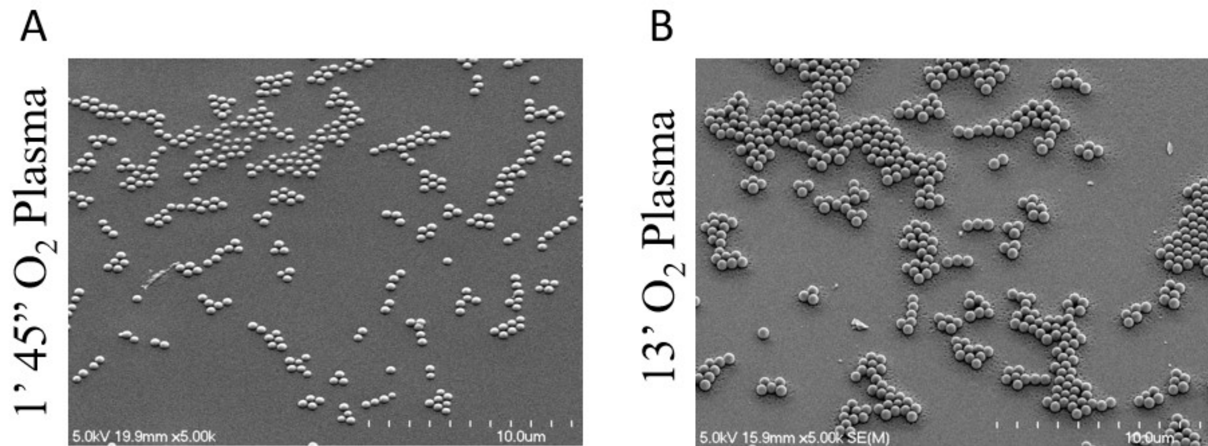

Figure S1. SEM images of PMMA coverage on SiO2NPs at a 45° angle after (A) 1'45" and (B) 13' exposure to O2 plasma.