

Supplementary Information for:

**Preparation and Measurement Methods for Studying Nanoparticle Aggregate
Surface Chemistry**

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TiO₂ Synthesis and Citrate Functionalization

TiO₂ nanoparticles (NPs) were synthesized following the method of Kotsokechagia, et al.¹ In a 250 mL round-bottom flask, 5 mL of TiCl₄ were added to 25 mL of anhydrous ethanol while stirring. After 2 min, 100 mL of anhydrous benzyl alcohol were added. The resulting yellow solution was stirred at 85 °C. For the NP batches used in this study, the corresponding solutions were heated for (6.5, 7, 10, and 14) h, respectively. After cooling to room temperature, diethyl ether was added to the nanoparticle suspension in a 2:1 volume fraction of ether:NP suspension, causing the NPs to concentrate to the bottom of the vessel. The NP mixture was then centrifuged at 5000 rotations per minute (r/min) (approximately 4000 g) for 10 min. The resulting supernatant liquid was removed and the remaining NPs were suspended via sonication in a 1:1 volume fraction mixture of deionized water:ethanol adjusted to pH = 1 using HCl.

The TiO₂ NPs were precipitated from the acidic storage solution by the addition of 3:1 diethyl ether and methanol. The cloudy precipitate was then agitated to completely homogenize the contents, followed by centrifugation (5000 r/min for 10 min), and decanting of the resulting supernatant. Sodium citrate (5 mmol/L in 18 MΩ-cm H₂O adjusted to a final pH of 5 using 0.5 mol/L NaOH) was added to the NP precipitate and the resulting mixture was agitated to free the precipitate from the bottom of the centrifuge tube. The suspension was sonicated for 1.5 h to yield a translucent suspension, which was then dialyzed using a cellulose membrane (Sigma Aldrich #D9777, molecular weight cut-off 12 400 Da) in 18 MΩ-cm H₂O for two 24 h periods. (Certain commercial equipment, instruments, or materials are identified to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement of the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose).

Determining TiO₂ Nanoparticle Dimensions and Phase

Scanning transmission electron microscopy (STEM) images were acquired in high-angle annular dark-field (HAADF) mode for all batches of NPs for the purpose of determining particle size. Fig. S1 shows representative images acquired for each respective NP batch, with all scalebars being 20 nm. Fig. S1b includes examples of lines drawn to measure the dimensions of each ellipsoidal particle. TEM Image and Analysis (TIA) software (FEI Company, Hillsboro, OR) was used for importing the raw STEM data files, drawing lines on individual particles, and measuring the NP dimensions. Because the particles were heavily agglomerated after drying on the TEM grid, 100 individual particles for each batch were selected from the HAADF images (multiple images taken per sample set) in such a manner as to conservatively pick particles that appeared well-delineated from neighbor particles, and subsequently both the long and short axis dimensions were recorded. Values for each dimension were averaged and the standard deviation calculated for each of the 100 NPs selected for each batch. While it's possible, due to orientation, that the long axis of the particle would be longer than what is recorded (for instance, if the particle was slightly tilted toward the electron beam such that the full profile was not normal), the minor axis dimension would always be correct. The sampling results suggest that the measurements for the major axis dimensions are accurate. This can be explained as the particles are more likely to lay down flat on the substrate due to local adhesion forces, meaning they would be presented in full profile to the electron beam. Additional STEM parameters are located in the Experimental Section of the manuscript text.

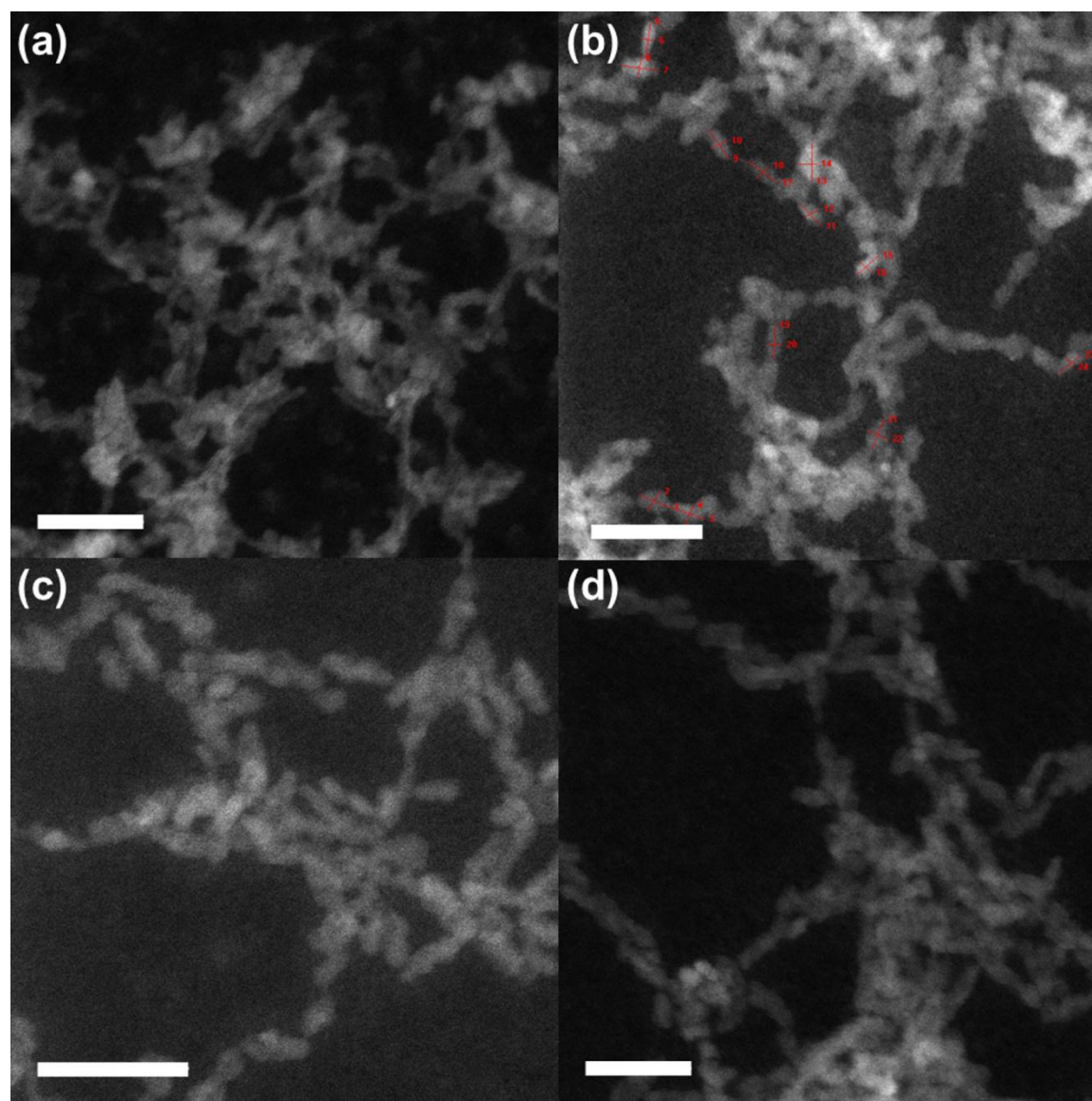


Fig. S1 Representative STEM images of each NP sample batch reacted for (a) 6.5 hr, Sample 1(b) 7 hr, Sample 2(c) 10 hr, Sample 3, and (d) 14 hr, Sample 4, reaction times. All scalebars are 20 nm. Using the TIA software, dimensions were determined to be $< 6.0 \text{ nm} \times < 3.0 \text{ nm}$, $6.2 \text{ nm} \times 3.3 \text{ nm}$, $6.1 \text{ nm} \times 2.9 \text{ nm}$, and $6.8 \text{ nm} \times 3.3 \text{ nm}$, respectively. Additional details and standard deviations reported in the manuscript text.

Selected-area electron diffraction (SAED) measurements were performed for each NP sample batch. Since Sample 1 had a different UV-vis absorbance spectrum Samples 2 through 4, we compared SAED images from NPs from Sample 1 and Sample 2 (the particles used in the NOM and pond water studies). Resulting SAED patterns are shown in Fig. S2. Crystal structure determination was carried out by measuring the ratio of the ring radii (which normalizes out

camera length, and therefore, scale effects) and comparing to the ratios of the known planar spacings of the commonly encountered TiO_2 phases of anatase, rutile, and brookite. The analysis conclusively showed that both NP Samples exhibited the structure of the anatase phase of TiO_2 , which rules out a change in crystalline structure as the origin for the different UV-vis spectrum measured for Sample 1.

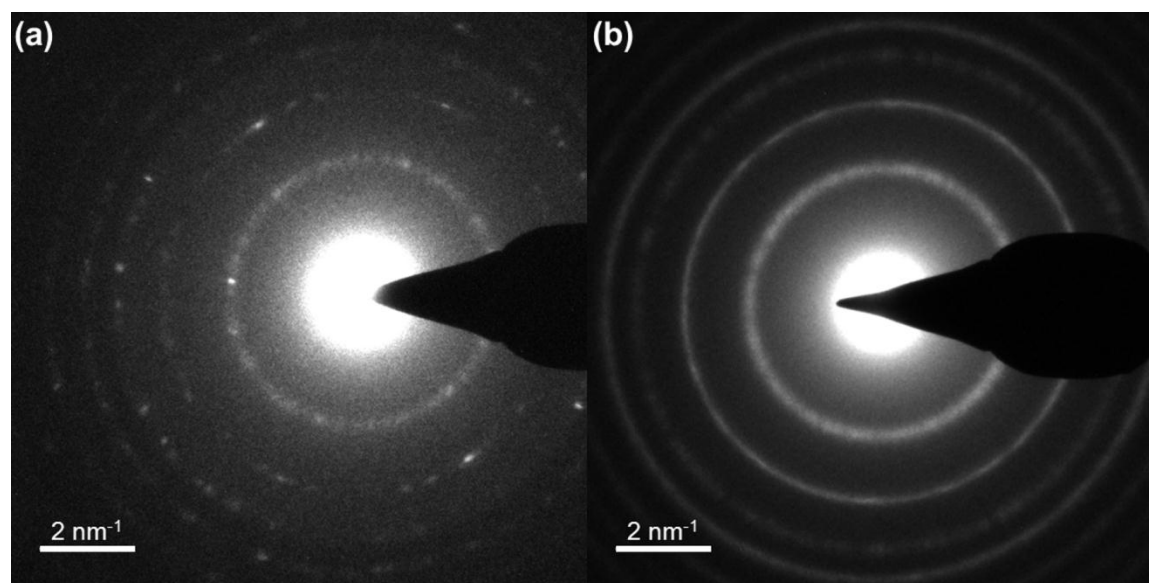


Fig. S2 SAED images for (a) the 6.5 hr NPs ($< 6.0 \text{ nm} \times < 3.0 \text{ nm}$; Sample 1), and (b) the 7 hr NPs ($6.2 \text{ nm} \times 3.3 \text{ nm}$, Sample 2). Analysis of both images conclusively shows that the TiO_2 NPs are anatase.

Monitoring of Inkjet Printing Enclosure for Potential NP Aerosol Formation

Inkjet printing with a piezoelectric drop-on-demand system deposited droplets of approximately 50 pL of solution onto the substrate, which evaporated very quickly once the deposition event was completed. The piezoelectric material generated a pressure pulse when a voltage was applied to the tip of the printer, dropping fluid at a frequency set by the user. If the entire droplet fully evaporated before hitting the substrate, the TiO_2 NPs could potentially form one aggregate still small enough to become aerosolized. TiO_2 NPs are considered nonhazardous

in solution, but potentially very hazardous if aerosolized. Proper precautions were taken to measure the possibility of aerosolizing particles while inkjet printing NP suspensions. A TSI 3760A condensation particle counter (TSI Incorporated, Shoreview, MN) was installed inside of the inkjet printer enclosure to determine if any NP aerosols were produced during NP deposition, drop splashing, or the transfer of dried NP deposits on the silicon substrates. No particles were detected from any of these events, but a SS-300-MS air filter system (Sentry Air Systems, Inc., Houston, TX), with a SS-300-PFP pre filter and a SS-300-HF High-Efficiency Particulate Air (HEPA) filter, was installed on the top portion of the JetLab 4 inkjet printer to remove the potential for any particles to be generated from inkjet printing of NP solutions.

Data Analysis Methods for ToF-SIMS Peak Identification and Peak Area Analysis

ToF-SIMS can generate mass spectra with mass resolutions of at least 4 000 $m/\Delta m$. Multiple full peak profiles can be present both above and below a nominal mass value. Therefore, an automated method was devised to accurately identify distinct peaks and calculate their respective peak areas for subsequent peak ratio analysis. SIMS spectra were batch-processed through a custom MATLAB, version R2010b, (Mathworks, Natick, MA) script to identify peaks at specific m/z ratios. Nominal m/z positions along the mass-to-charge axis for all desired masses were input into the script. All peak areas were calculated with raw data signals, but since ToF-SIMS data have Poisson noise fluctuations across each peak, the raw mass spectral data were smoothed for the sole purpose of identifying more accurate peak bounds. To locate specific peaks, the custom-written code examined a 0.5 m/z window in the mass spectrum around each input mass value. All peaks in this mass window were identified by sweeping a top-hat filter across the region with a variable m/z width, such that it was 0.017 at 15 m/z and 0.051 at

400 m/z . This is to account for the fact that peaks can broaden with increasing m/z value. Once the maximum intensity and center m/z were located for all found peaks in the mass window, the code stepped both left and right of each found peak center in similarly changing mass-based increments to identify the respective peak bounds. This search ended either when the minimum found intensity was less than 1% of the maximum intensity of that peak, or if a neighboring peak was detected. For this latter case, the code selected a m/z point at the minimum intensity between the two peaks, excluding the neighboring peak from the area analysis. The minimum intensities on each side of the peak center became the peak bounds. From these endpoint values, each peak area was determined by finding the Riemann sum of the raw (unsmoothed) data. Spectrum file names and the list of peak areas were saved to a text file which could easily be imported into a spreadsheet for further analysis for as many masses and files as were selected. The complete peak identification and peak area determination script will be available upon request.

ToF-SIMS Background Mass Spectrum on Silicon Without TiO₂ NPs

A ToF-SIMS mass spectrum is included here to directly compare with that of manuscript text Fig. 5. The region of $40 \leq m/z \leq 70$ shown in Fig. S3 encompasses the part of the mass spectrum where the $C_3H_5^+$ (m/z 41.05), Ti^+ (m/z 47.95), and TiO^+ (m/z 63.95) are located. The acquisition was on a piece of silicon where no inkjet printing of TiO₂ NPs occurred. The background level is sufficiently low to properly detect Ti^+ and TiO^+ in the desired sample systems.

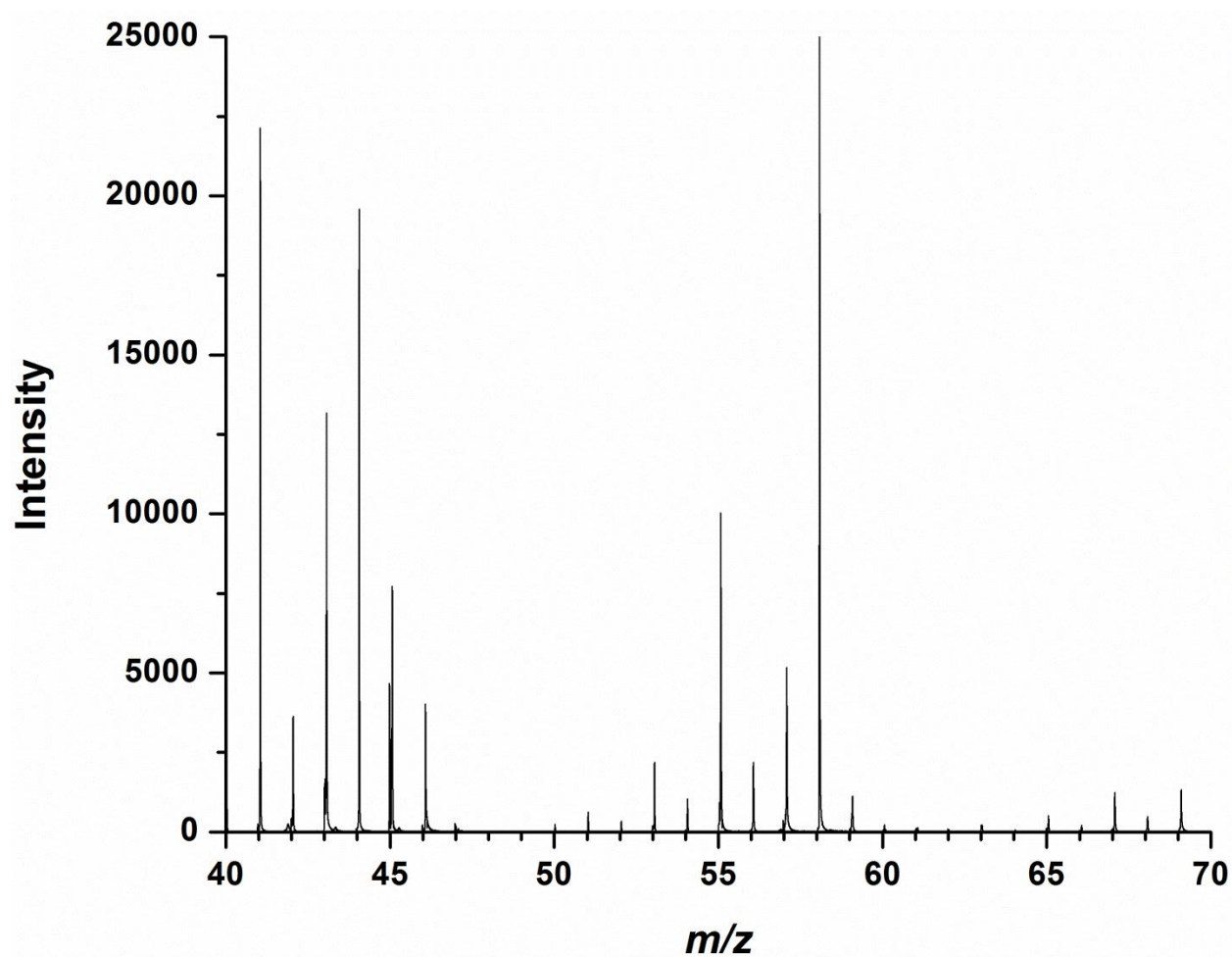


Fig. S3 ToF-SIMS background mass spectrum on piece of silicon without deposited TiO₂ NPs.

References

1. Kotsokechagia, T.; Cellesi, F.; Thomas, A.; Niederberger, M.; Tirelli, N. Preparation of ligand-free TiO₂ (anatase) nanoparticles through a nonaqueous process and their surface functionalization. *Langmuir* **2008**, 24 (13), 6988-6997.