Supplementary Information

Nanomechanical Mapping of a High Curvature Polymer Brush Grafted from a Rigid Nanoparticle

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General Image Acquisition Settings

The piezo was modulated at a frequency of 2 kHz with an amplitude of 100 nm, that is force vs. separation data was collected every 0.5 ms. The aspect ratio in all images was 1:1 with the

images obtained by a tip scanning from right to left in the frame of the image, and bottom to top in Figs. 1-5, except in Fig. 4 where the tip direction was top to bottom.

Figure Specific Acquisition Settings

Figure 1 D-F

Instrument Settings

The scan size was 1.10 μm with a scan rate of 0.98 Hz, resulting in 2.00 cycles of force vs. separation data per pixel with a pixel resolution of 2.15 nm. The spring constant was calibrated to 1.12 Nm^{-1} using a deflection sensitivity of 12.85 nmV^{-1} found as the inverse of the slope of the hard wall interaction region in the force vs. distance data, calibrated against silica in water. A peak force setpoint of 5 nN was used. The Z-limit, which sets the maximum allowable voltage and thereby the resolution in the vertical direction, was set to its default value, yielding a typical digital height resolution of less than 1 Å. In the ScanAsyst software, the feedback gain was set to auto due to regions of both flat topography and high curvature. The deformation fit region was set to its default value 85%.

Acquisition Conditions

The images (512×512 pixels) were acquired in 1 mM NaCl solution with the pH of the injected solution set to 9.24 prior to measurement. An injection volume of 5 mL was used where the excess volume passed through an outlet to a waste container.

Data Processing

Recorded raw data were visualized in the NanoScope Analysis (v 1.20) software. Recorded data were subjected to subtraction of a first order polynomial fit in the horizontal direction

and centered around the mean in order to remove tilt. While removing tilt, asymmetric features can cause artefacts in the resulting image since the asymmetric features affect the baseline and thereby the resulting fit. A cutoff was used in order to remove these effects while maintaining a proper fit to the baseline data. The cutoff, ignoring data above, in baseline fitting was for Fig. 1D (Height) 5%, Fig. 1E (Deformation) 5% and Fig. 1F (Dissipation) 15%. The resulting data after subtraction of the best polynomial fit were exported in ASCII format and imported in MATLAB® to produce gray scale coded images. The display range for Figure 1D (Height) is 0 to 25 nm (data range: -3.5 to 34.4 nm). The display range for Figure 1E (Deformation) was adjusted to 2.7 to 15 nm from the full data range (2.7 nm to 44.2 nm) due to a single spot outlier. The display range for Figure 1E (Dissipation) was, in units of eV, 147 to 600 eV (data range: 147 to 1056 eV) converted to units of kT using k= 8.617×10^{-5} eV K^{-1} and T=295 K.

Figure 2

Instrument Settings

The scan size was 321 nm with a scan rate of 0.98 Hz, resulting in 2.00 cycles of force vs. separation data per pixel with a pixel resolution of 0.63 nm. The spring constant was calibrated to 0.88 Nm^{-1} using a deflection sensitivity of 13.86 nmV^{-1}. The setpoint forces were 2, 7, 10, and 2 nN. The Z-limit was set to its default value, yielding a typical digital height resolution of less than 1 Å. In the ScanAsyst software, the feedback gain was set to auto due to regions of both flat topography and high curvature. The deformation fit region was set to its default value 85%.

Acquisition Conditions

The images (512×512 pixels) were acquired in 1 mM NaCl solution with the pH of the injected solution set to 9.24 prior to measurement. An injection volume of 5 mL was used where the excess volume passed an outlet to a waste container.

Data Processing

Recorded raw data were visualized in the NanoScope Analysis (v 1.20) software and the data was exported in ASCII format and further treated in MATLAB®. Recorded data were subjected to subtraction of a first order polynomial fit in the horizontal direction and centered around the mean in order to remove tilt. The cutoff, ignoring data above, in baseline fitting is summarized in Table S1 below:

Table S1. Cut off values used for baseline fitting of first order polynomials to remove tilt.

Cutoff	2 nN	7 nN	10 nN	2 nN back
Height	0.1	0.1	0.1	0.1
Deformation	0.2	0.2	0.2	0.3
Adhesion	0.57	0.5	0.5	0.5
Dissipation	0.5	0.32	0.3	0.55

In the ScanAsyst software, the feedback gain was set to auto due to regions of both flat topography and high curvature. The deformation fit region was set to its default value 85%.

Figure 4

Instrument Settings

The scan size was 150 nm with a scan rate of 0.98 Hz, resulting in 2.00 cycles of force vs. separation data per pixel with a pixel resolution of 0.29 nm. The spring constant was calibrated to 1.12 Nm^{-1} using a deflection sensitivity of 12.85 nmV^{-1}. The setpoint force was 6 nN. The Z-limit was set to its default value, yielding a typical digital height resolution of less than 1 Å. In the ScanAsyst software, the feedback gain was set to auto due to regions of both flat topography and high curvature. The deformation fit region was set to its default value 85%.

Acquisition Conditions

The images (512×512 pixels) were acquired in 1 mM NaCl solution with the pH of the injected solution set to 6.1 prior to measurement. An injection volume of 5 mL was used where the excess volume passed through an outlet to a waste container.

Data Processing

Recorded raw data were visualized in the NanoScope Analysis (v 1.20) software and the data was exported in ASCII format and further treated in MATLAB®. Recorded data were subjected to subtraction of a first order polynomial fit in the horizontal direction and centered around the mean in order to remove tilt. The cutoff, ignoring data above for the fitting, was for height 5%, deformation 20%, adhesion 20% and dissipation 34%. The display range in the left panel corresponds to the full data range and is for height -1.2 to 16.1 nm, deformation 3.0 to 8.7 nm, adhesion 0.0 to 1.1 nN and dissipation -20 to 153 eV, converted to units of kT using k= 8.617×10^{-5} eV K^{-1} and T=295 K.

Figure 5

Instrument Settings

The scan size was 153.1 nm with a scan rate of 0.98 Hz resulting in 2.00 cycles of force vs. separation data per pixel with a pixel resolution of 0.30 nm. The spring constant was calibrated to 0.55 Nm^{-1} using a deflection sensitivity of 19.92 nmV^{-1}. The setpoint force was 6 nN. The Z-limit was set to its default value, yielding a typical digital height resolution of less than 1 Å. In the ScanAsyst software, the feedback gain was set to auto due to regions of both flat topography and high curvature. The deformation fit region was set to its default value 85%.

Acquisition Conditions

The images (512×512 pixels) were acquired in 1 mM NaCl solution with the pH of the injected solution set to 9.2 prior to measurement. An injection volume of 5 mL was used where the excess volume passed through an outlet to a waste container.

Data Processing

Recorded raw data were visualized in the NanoScope Analysis (v 1.20) software and the data was exported in ASCII format and further treated in MATLAB®. Recorded data were subjected to subtraction of a first order polynomial fit in the horizontal direction and centered around the mean in order to remove tilt. The cut off, ignoring data above for the fitting, was for height 10%, deformation 20%, adhesion 20% and dissipation 40%. The display range in the left panel corresponds to the full data range and is for height -1.0 to 20.4 nm, deformation 0.8 to 10.7 nm, adhesion -0.1 to 0.8 nN and dissipation 12 to 339 eV, converted to units of kT using k= 8.617×10^{-5} eV K^{-1} and T=295 K.

Figure 6

Instrument Settings

The scan size was 150 nm with a scan rate of 0.50 Hz, resulting in 3.90 cycles of force vs. separation data per pixel with a pixel resolution of 0.29 nm. The spring constant was calibrated to 0.88 Nm^{-1} using a deflection sensitivity of 13.86 nmV^{-1}. A setpoint force of 2 nN was used. The Z-limit was 2.0 μm, yielding a typical digital height resolution of less than 0.4 Å. In the ScanAsyst software, the feedback gain was manually adjusted to 9 since the scanned area was dominated by high curvature. This value resulted in low force error without increasing the noise in the force error signal. The deformation fit region was set to its default value 85%. Force vs. separation data was saved using the High Speed Data Capture (HSDC) command which enables the user to save raw data in the form of force vs. separation. The deflection error and the height were captured at a rate of 500 kHz during 2996 ms at Y-line position 183 (of 512).

Acquisition Conditions

The data was acquired in 1 mM NaCl solution with the pH of the injected solution set to 9.24 prior to measurement. An injection volume of 5 mL was used where the excess volume passed through an outlet to a waste container.

Data Processing

Force vs. separation data was visualized using the NanoScope Analysis (v. 1.20) software and the data was exported in ASCII format. Force vs. separation was plotted directly in MATLAB® as a function of the position of the nanoparticle center on approach (top left) and retraction (top right) as an average of 8 cycles (4+4 for scan direction left-to-right and right-to-left respectively). Force vs. separation data (A and B) were visualized from 0 to 20 nm separation using interpolated shading, color map gray, axis option vis3d and -38 and 30

degrees horizontal rotation and vertical elevation respectively. Superimposed contour lines show the force at 250, 750, 1250 and 1750 pN respectively. Force vs. separation data (C) were selected from the particle edge and center. A zero-force baseline was introduced as a guide to the eye.

Force Error Analysis

The error in the force may affect the nanomechanical properties and thus the force error images were examined. In this case, the error for the data in Fig. 2 with a 2 nN peak force setpoint is: 65±54 pN (3%) at the edge and 40±30 pN (2%) at the center; with a 7 nN peak force setpoint: 102±99 pN (1%) at the edge and 38±7 pN (<1%) at the center; with a 10 nN peak force setpoint: 122±120 pN (1%) at the edge and 16±8 pN (<1%) at the center; for the return to a 2 nN peak force setpoint: 69±51 pN (3%) at the edge and 30±7 pN (2%) at the center. In Fig. 4, the error is 162±119 pN (3%) at the edge and 73±54 pN (1%) at the center, and in Fig. 5 it is 137±105 pN (2%) at the edge and 28±18 pN (<1%) at the center.

Tip imaging

The tip qualification procedure in the NanoscopeAnalysis Software (v. 1.20) from Bruker was used to create a tip image using a titanium roughness sample containing sharp edges (model number RS-15M, Bruker). The roughness sample was imaged over an area of 1×1 μm to produce a height image of 512x512 pixels. Local maxima within the height image were searched to produce local peaks within 10x10 nm sub-squares (see Figure S1, left). The slopes of all the peaks were calculated and the steepest slope in any direction constituted the slope in the tip-image (see Fig. S1, right) since no slope can be steeper than that of the tip.

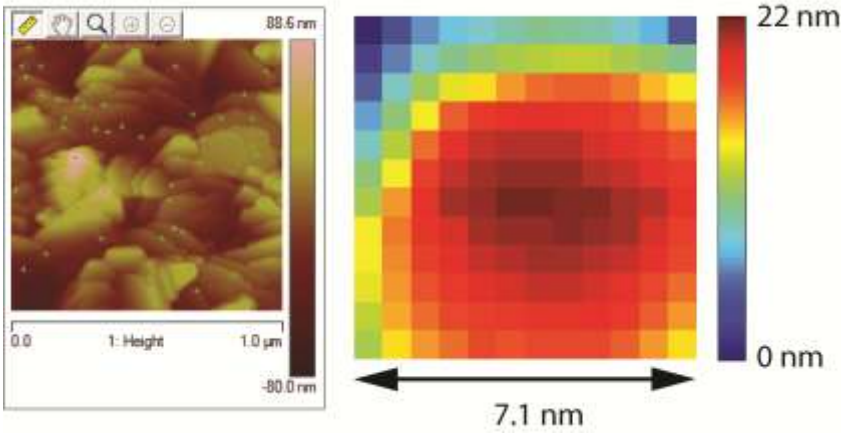

Figure S1. Left: Height image from a 1×1 µm scan showing local maxima used to determine the tip shape. Right: resulting tip shape.

Tip Asymmetry Effect on Property Mapping: Image Asymmetry.

We note in the main paper that although each deformation, adhesion and dissipation map displayed in Figs.1, 4 and 5 showed a local minimum in the centre surrounded by a maximum at a horizontal position further out, the images do not all appear symmetrical. We consider first whether image asymmetry is an artifact of the variation of peak force setpoint error relative to the scan direction (see Fig. 1C). Most notably, the peak force was overshot as the tip first approached the particle from the bare surface, as the feedback control system could not perfectly maintain the applied peak force at a constant value. The feedback correction restored the peak force to the setpoint as the tip scanned across the particle, but then a somewhat too low peak force was applied as the tip then moved away from the particle centre as the feedback control imperfectly adapts to the changing force profiles. The maximum error amounted to only 3% of the peak force setpoint. Thus, there could be systematic error in the magnitudes of the properties reported on different sides of the nanoparticles, but the variation in the reported properties from the particle centre to the extremities are larger than can be attributed to this small systematic error in applied load.

From the data in Fig. 6A, where the force vs. separation curves are plotted for all horizontal positions, we can estimate the maximum error in the deformation for a single force curve based on a given peak force setpoint error. A 3% peak force setpoint error near the edges (shown by the "ridges" in the three-dimensional force curve representation) would cause an error of 0.13 nm or 2.7% error in deformation. For the largest error in peak force recorded in any individual measurement, 10.4%, the resulting deviation in height would be 0.31 nm or 1.8%. Note that the error in height approaches zero as hard-wall contact is approached, meaning for higher forces, the difference in height would be even less. Given the small error in deformation and height, it is unlikely that the adhesion or the dissipation will suffer significantly larger error. Asymmetry is not likely due to peak force error, nor is it likely to be an effect of the scanning angle, since the tip will always have the same geometry relative to the surface.

Next, we consider whether the image asymmetry is an artifact of the tip-shape. In Fig. S2 the deformation is shown as a line scan over the nanoparticle at pH 9.2 at peak forces of 2 nN, 7 nN, 10 nN and 2 nN as a repeat measurement. There is a trend of higher deformation on the left side of the nanoparticle. We propose that this is due to a relatively higher contact area on the left side of the tip (see Fig. S1), as a result of the tilt of the tip as mounted in the probe holder.

The difference in the maximum deformation between each side increases with peak force. The asymmetry in the tip-shape, which most likely is caused by a finite tilt-angle of the mounted cantilever in the probe holder, shows a steeper slope to the left side of the tip apex compared to the right side. The increased deformation on the left side in the raw data could be explained by the relatively smaller contact area made between the right side of the tip and the left side of the particle as the tip moves away from the particle during a scan. Higher deformation on the left-hand side of the nanoparticle is also present in Fig. 4 and Fig. 5. In

these cases, different tips were used but the same behavior is repeated. Thus, this further corroborates the idea that the deformation asymmetry is caused by the mounting tilt-angle. Inspection of adhesion or dissipation raw data used to produce the property maps does not reveal any pronounced asymmetry in the data. Therefore, it is plausible to propose that data asymmetry mainly relates to deformation and is an effect of the tip-tilt angle.

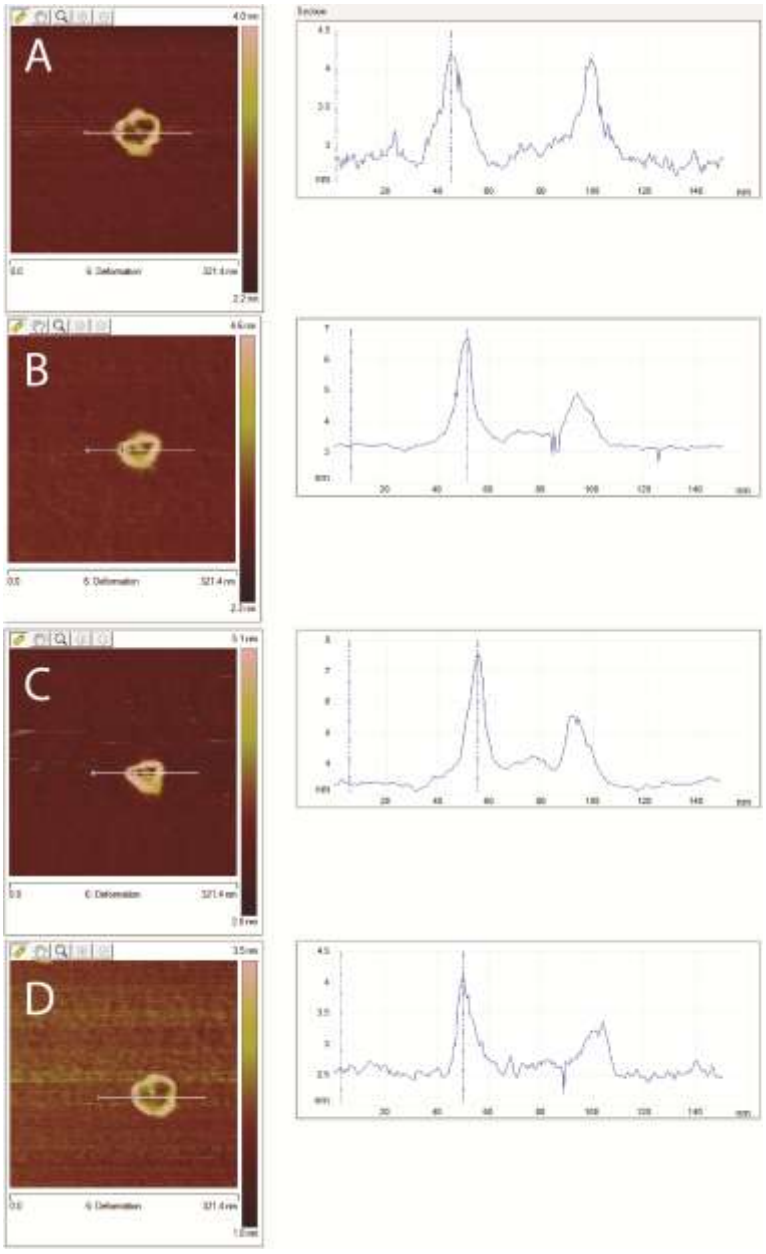

Figure S2. Deformation raw data and corresponding section profiles at a peak force of 2 nN (A), 7 nN (B), 10 nN (C) and 2 nN repeat (D).

In Fig. S3, force vs. separation data are shown as a function of the horizontal distance to the nanoparticle centre on approach of the tip to the sample. From the isodynamic curves in the top view, it is seen that the range of the steric force is longer on the left side of the nanoparticle than on the right side, consistent with greater deformation on the left.

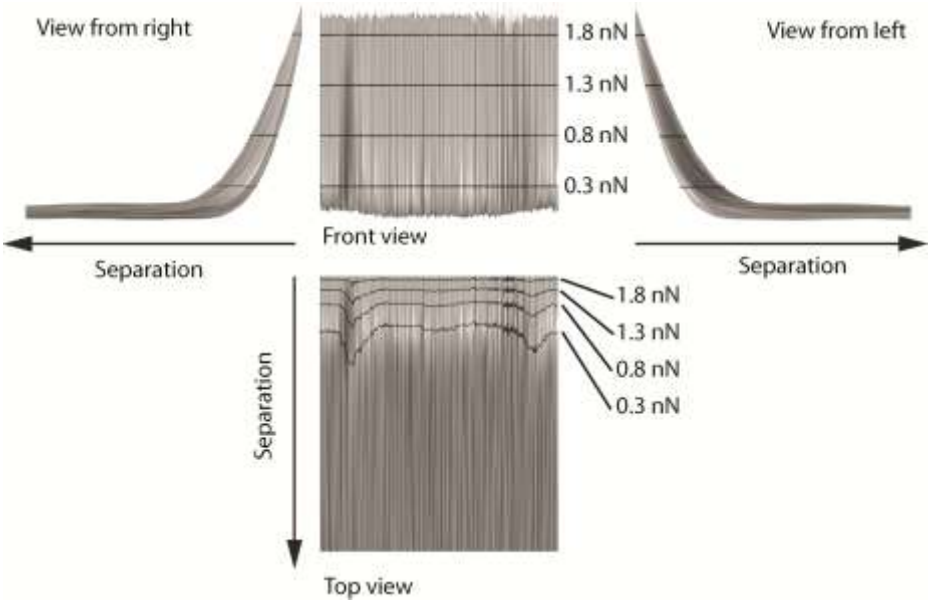

Figure S3. Force vs. separation curves plotted as a function of the horizontal distance to the nanoparticle centre on approach of the tip to the sample. Isodynamic curves show where the force was 0.3 nN, 0.8 nN, 1.3 nN and 1.8 nN respectively. A peak force of 2 nN was used and the data was recorded at pH 9.2 in 1 mM NaCl at 23°C.