***Atomic Force Microscopy*.**

***Experimental setup*.** The experimental setup used for these studies has been described before.[1] Asylum Research MFP-3D AFM instrument was coupled with a custom build environmental cell was used to investigate $CaCO_3$ $(10\bar{1}4)$ surfaces at controlled relative humidity. It consists of: (*i*) gas handling system to control relative humidity, (*ii*) an environmental cell connected to the scanner head and coupled to sample heater/cooler and, (*iii*) environmental conditions monitoring and control system. A schematic of the apparatus is shown in Figure 1a. To prepare a gas flow stream of known relative humidity, dry nitrogen is passed through Erlenmeyer flask filled with water. Polypropylene tubing is used to transport nitrogen and was not submerged into water, not to induce scanning artifacts due to the acoustic waves from gas bubbling. The flow of nitrogen gas is regulated using two rotameters (Cole Parmer, max flow of air 61 mL/min). Nitrogen flow to the environmental cell was kept ~40 mL/min and adjusted as needed to maintain constant relative humidity.

The environmental cell, ~6 cm^3 in volume, contains a heater/cooler element as well as RH/temperature sensor magnetically attached to the horizontal heater/cooler element. The sample is mounted on a stainless steel puck which is magnetically attached to the heater/cooler element. The environmental cell is connected to an AFM scanner head via flexible bellows and sealed with a Viton ring. Relative humidity and temperature inside of the closed cell is monitored using a model HIH3610 relative humidity sensor from Honeywell Inc with 2% accuracy at 298 K which is magnetically attached to the heater/cooler element. Thus, all of the relative humidity values reported in this paper are accurate within 2%. The linearity of the relative humidity sensor is checked against saturated salt solutions of know relative humidity: LiCl (11% RH), K_2CO_3 (43% RH) and NaCl (75% RH).[2] The heater/cooler element utilizes a

Peltier thermoelectric device to achieve an operating temperature range 253 to 393 K. Both temperature and relative humidity are controlled using a separate heater controller (MFP-3D Heater Controller) from Asylum Research, which is connected to the main MFP-3D controller. Relative humidity as well as heater/cooler temperature run through the Asylum Research MFP3D software (version 070111+830), embedded into Igor Pro (version 6.03) software. The same software was used to measure area and volume of particles.

To minimize any extraneous vibrational interference Herzan TS-150 active vibration isolation table is used. The entire system is in Herzan acoustic enclosure to ensure thermal and vibrational stability during experiments.

Cantilever force constant calibration. Low force constant Si cantilevers were used (CSC37/AlBS from MikroMash, cantilever A with a typical force constant of 1.2 N/m) to minimize any tip effects on the surface. The cantilever force constant was calibrated against initial unreacted $CaCO_3$ surfaces using the following method. First, a force plot (tip displacement in z axis vs deflection volt) was acquired using low deflection values as a trigger point (less than 5nN). From the obtained force plot, the Inverse Optical Lever Sensitivity (InvOLS) is calibrated using the slope of the retraction curve. InvOLS has units of nm/V and converts the cantilever deflection from volts to meters. A typical InvOLS value for cantilevers used in this work was ~80 nm/V. The force constant of the cantilever is then found using fit parameters of a single harmonic oscillator (SHO) response function. In particular, thermal method is used that takes advantage of the equipartition theorem applied to the cantilever potential energy (1)[3,4]

$$\frac{1}{2}k_B T = \frac{1}{2}k\left\langle x^2 \right\rangle \quad (1),$$

so that

$$k = \frac{k_B T}{\langle x^2 \rangle} \qquad (2)$$

where k_B is Boltzmann's constant, T is the absolute temperature, k is the spring constant and x^2 is the mean square cantilever displacement. $\langle x^2 \rangle$ in (2) can be calculated using a thermal fit procedure (3):[4]

$$\langle x^2 \rangle = \left(\frac{\pi}{2}\right) \upsilon_0 Q A_{dc}^2 \qquad (3),$$

where υ_0 is a resonant frequency, Q is the quality factor of the SHO peak and A_{dc} is dc amplitude. Thermal excitation behaves as a flat white-noise driving force, so the SHO can be approximated by an amplitude response function which, in turn, can be recorded using Asylum Research MFP3D software (version 070111+830) software. Once an amplitude response function has been acquired, it is fitted and υ_0, Q and A_{dc} values are obtained from the fit. Using those, x^2 following with k (cantilever force constant) can be calculated. Having both k and InvOLS, the force on the sample during imaging can be estimated from (4)

$$F = - k \cdot InvOLS \cdot (DeflectionSetpoint – FreeDeflection) \qquad (4)$$

where DeflectionSetpoint is the feedback setpoint in volts and FreeDeflection is the deflection in volts when the tip is above the sample.

AC imaging and phase shift. Alternating current (AC) imaging mode was used in all experiments. The cantilever amplitude set point was always set to exert less than 10 nN of force as determined from the force calibration measurements. At the beginning of the experiment large area (15x15 μm) was scanned to locate a region of interest. Smaller area (~3x3 μm) was further scanned continuously over the period of several hours to monitor surface changes.

Typically, 70% RH was used in these experiments. Images were acquired using 512x512 resolution were acquired.

Phase imaging combined with AC mode AFM can provide spatially resolved information barely visible in topography or amplitude images.[5] Those include variations in physical and chemical properties, friction, composition, elasticity and adhesion, to name a few. A lock-in amplifier is used to extract the phase information in AC mode. For this, an oscillating voltage is applied to oscillate the piezo element connected to the cantilever, which then is driven at a resonant frequency ω:

$$V_d \cdot \cos(\omega t) \qquad (5)$$

where V_d is drive voltage, ω – drive frequency and t – time. Cantilever oscillates at a given amplitude and phase shift, ϕ, relative to the drive. The oscillation is measured as the response voltage, V_{resp}, by the Position Sensitive Detector (PSD) which provides an oscillation signal in form of Eq 6:

$$V_{resp} \cdot \cos(\omega t + \varphi) \qquad (6).$$

To extract the phase signal, the response signal detected by PSD in Eq 6 is multiplied by the oscillating piezo drive voltage Eq 5:

$$V_{resp} \cdot \cos(\omega t + \varphi) \cdot V_d \cdot \cos(\omega t) = 1/2 \cdot V_{resp} \cdot V_d \cdot [\cos(2\omega t + \varphi) + \cos\varphi] \qquad (7).$$

When the signal is low-pass filtered the resulting dc component contains a term proportional to the cosine of the phase:

$$\bar{i} = 1/2 \cdot V_{resp} \cdot V_d \cdot \cos\varphi \qquad (8).$$

$\bar{i}$ is referred to as the "in-phase" component. Additionally, "quadrature component, $\bar{q}$, can be obtained by multiplying the cantilever response by $V_d \cdot \sin(\omega t)$ term:

$$\bar{q} = -1/2 \cdot V_{resp} \cdot V_d \cdot \sin\varphi \,. \quad (9)$$

These two quantities combined are used to extract both the cantilever amplitude, A, and phase, ϕ:

$$A = \sqrt{\bar{i}^2 + \bar{q}^2} \quad (10)$$

$$\varphi = \tan^{-1}\frac{\bar{q}}{\bar{i}} \quad (11).$$

In all experiments, images were acquired in a repulsive AC mode, e.g. phase shift between drive (V_d) and response (V_{resp}) was negative. This was controlled by centering phase at 90^o and always having phase value during the scan below 90^o. In this regime the average interaction force between the tip and the sample is repulsive.[6,7] By setting up the proper value of the tip deflection, repulsive regime can be maintained. In majority of experiments phase value of $\sim 70^o$ was maintained.

References

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