Video-Rate AFM Opens New Research Possibilities into Surfactant Behavior at Solid-Liquid Interfaces

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Introduction

Surfactants have many important industrial applications including stabilization of colloidal dispersions, corrosion inhibition, and lubrication.[1] Their formation of ordered colloidal structures (micelles) on surfaces also makes them attractive as templates for creating nanostructures.[2,3] To use surfactants successfully for all these purposes, it is important to fully understand their behavior at solid-liquid interfaces.

Cetyl trimethylammonium bromide (CTAB) is a surfactant known to form micelles in solution. It also spontaneously self-assembles into rows of hemicylindrical structures, or hemimicelles, upon adsorption at the solid-liquid interface with highly oriented pyrolytic graphite (HOPG).[4] Figure 1 shows a schematic diagram of how the surfactant molecules assemble with their polar headgroups exposed to the solution and their hydrophobic tails packed in the interior of the hemimicelles.

It has been shown that these structures exhibit dynamic behavior, not just during their initial formation but also in response to mechanical or chemical perturbations.[1,5] Therefore, a more complete understanding of their dynamic behavior may help guide their use in practical applications. The enhanced capabilities of new atomic force microscopes (AFMs) enable imaging with more spatial and temporal detail than ever before. Here, we describe experiments using high-resolution, video-rate AFM imaging to study the dynamics of CTAB hemimicelles formed at the HOPG-solution interface.

AFM Imaging of Surfactant Structures

AFMs are powerful tools for studying surfactant structures at liquid-solid interfaces. Unlike scanning electron microscopes, AFMs can image with high spatial resolution while operating in liquid. In fact, hemimicelles were first successfully imaged with an AFM more than 20 years ago.[6] That work finally allowed the surfactant structures to be directly visualized and compared to predictions. However, conventional AFMs used then, and even today, take several minutes to capture a single image. At such slow imaging rates, the structures appear static. Only by comparing adjacent scan lines could researchers begin to infer that tip-induced defects "heal" on the order of milliseconds.[1]

In 2008, a new generation of "fast-scanning" AFMs emerged with the release of the first Asylum Research Cypher AFM. Though 10-20× faster than conventional AFMs, the timescales of dynamic events such as hemimicelle aggregation still exceed their temporal resolution. Therefore, some researchers have resorted to building their own, much faster AFMs.[7] Many impressive results have been obtained with such AFMs,[8] but they clearly represent a high barrier for researchers not focused on AFM instrument development.

That barrier was removed in 2017 with Asylum Research's introduction of the Cypher VRS, the world's first and only full-featured video-rate AFM. It enables high-resolution imaging at line rates up to 625 Hz, which means that dynamic events can now

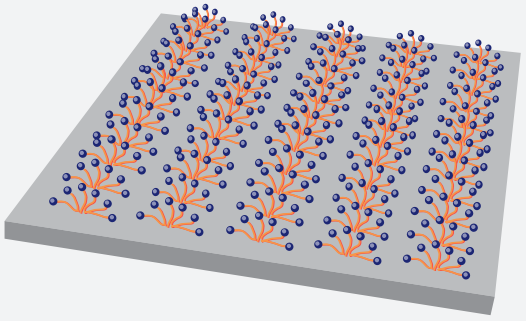

Figure 1: Schematic diagram of CTAB hemimicelles on HOPG

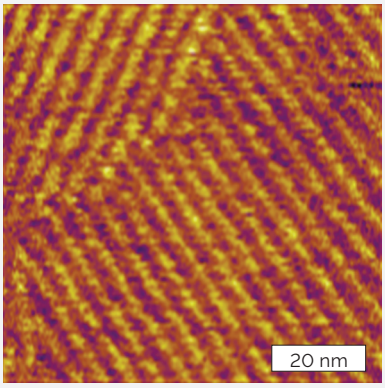

Figure 2: Single frame taken from a video captured at 5.8 fps (173 ms per frame), clearly showing the rows of CTAB hemimicelles on the HOPG surface and the orientation of the domain boundaries. Tapping mode phase data is shown here for optimum contrast. Watch the full video: http://AFM.oxinst.com/CTAB

be monitored at frame rates in excess of 10 frames per second (fps). Though other AFMs have reached similar speeds,[7] the Cypher VRS is the first to provide this capability on an easy-to-use AFM that also offers a full range of modes and environmental control options. It is now possible to obtain images of CTAB hemimicelles with both high spatial resolution and high speed. An example of these new capabilities is shown in Figure 2, where hemimicelles are clearly evident.

Materials and Methods

For all experiments shown here, samples were prepared by introducing a 5 mM CTAB solution onto a freshly cleaved HOPG substrate. Once imaging had commenced, the dynamic rearrangement of the micelle structure was initiated by introducing 10% isopropyl alcohol via syringe pump at a rate of 2.4 to 6 mL/h while imaging continuously.

All imaging was done on a Cypher VRS AFM (Oxford Instruments Asylum Research) at ambient temperature with Olympus AC10DS probes in tapping mode. These probes feature small cantilevers measuring just 2 µm in width and 9 µm long. The relatively high resonance frequency in liquid (~450 kHz) of these small cantilevers and their low quality factor (Q) contribute to the higher system bandwidth that allows video-rate imaging. All images shown here are frames selected from movies created by continuous scanning at rates between 0.5 and 5.8 fps. The tapping mode phase data is shown because it provides clearer contrast of micelle structure than the topography (height) data.

Photothermal excitation (blueDrive™) was used to excite the cantilever resonance for tapping mode imaging instead of the conventional approach of piezoacoustic excitation. Photothermal excitation provides a much cleaner drive response in liquid,

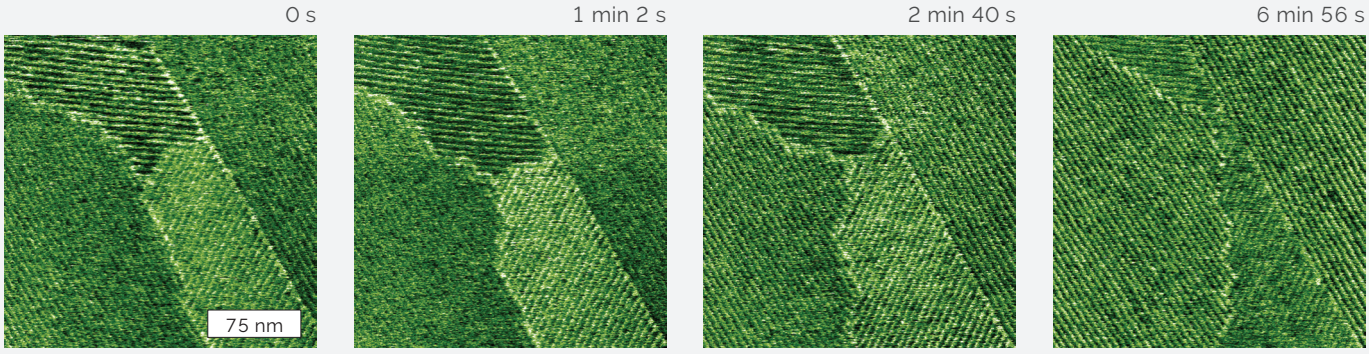

Figure 3: Sequence of selected frames from a 0.48 fps (250 Hz line rate) video showing two CTAB grains of opposite row orientation (upper-left and lower-right) bounded on the left and right by two grains with parallel orientation. Over time, the two grains narrow at their boundary, eventually separating and drifting apart while the adjacent grains on the left and right merge together. Note the three different row orientations, corresponding to the three directions perpendicular to the HOPG symmetry axes. Though one can appreciate the overall evolution of the grain structure from these four images, the full video shows the process in far greater detail. See it at: http://AFM.oxinst.com/CTAB

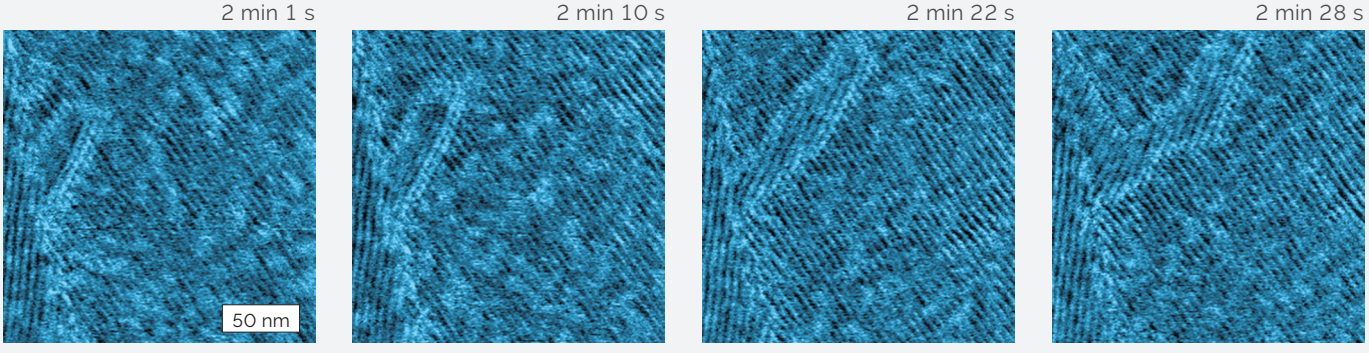

Figure 4: Sequence of selected frames from a different video captured at 0.95 fps (250 Hz line rate) showing the spontaneous formation of a narrow CTAB grain along the boundary of two orientation domains (upper left). The grain continues to grow for about 20 s until a broader grain in the same orientation begins to emerge behind it. The full video shows that this new grain continues to grow and push the smaller grain out of the field of view. See the full video at: http://AFM.oxinst.com/CTAB

which makes it easy to find and tune the resonance. Even more importantly, the photothermal drive response remains constant with time and irrespective of the fluid volume. This makes it possible to maintain uninterrupted imaging for the entire length of the experiments, even during continuous fluid perfusion.

Results and Discussion

Figures 3 to 5 show sequences of images taken over somewhat larger scan sizes than that in Figure 2. The broader field of view better captures the multiple grains (regions of uniform orientation) formed by CTAB and the boundaries that separate them. Because each video is several minutes long and thus consists of hundreds of frames, only several frames from a shorter time span can be shown here (see links to full movies). Though at Asylum Research we take pride in our technical leadership in AFM instrumentation, we certainly are not experts in the dynamics of surfactant self-assembly. Thus the images here are meant simply to indicate the sort of observations that are possible with the Cypher VRS.

In Figure 3, for instance, we see four distinct grains where the micelles have different angular orientations. Over the span of time covered by these frames, the grain boundaries significantly shift; but the micelles within each grain maintain their orientation. Figure 4 shows a slightly different process, wherein a new grain emerges at the boundary between two pre-existing grains. Conversely, Figure 5 shows small structures absorbing and disappearing into the larger surrounding grains. These events and others shown in the full videos take place on a time scale much shorter than the typical image acquisition time of a conventional AFM. Only by imaging with a video-rate AFM can these processes be clearly visualized.

Though we offer no interpretation here, these examples demonstrate the ability to visualize and monitor the time-course evolution of the micelle grains. For instance, one could readily analyze the edge velocity of a grain or even the areal rate of change of grain size in addition to angular orientation. By monitoring both topography and phase, one can observe interesting phenomena where the micelle grains sometimes seem to be pinned at step edges in the HOPG, and other times when they flow across the steps as if they were not there. In short, there appear to be many opportunities to learn more about the dynamics of these and other similar systems. We invite researchers in the field to contact us to discuss these exciting possibilities and learn more about the Cypher VRS.

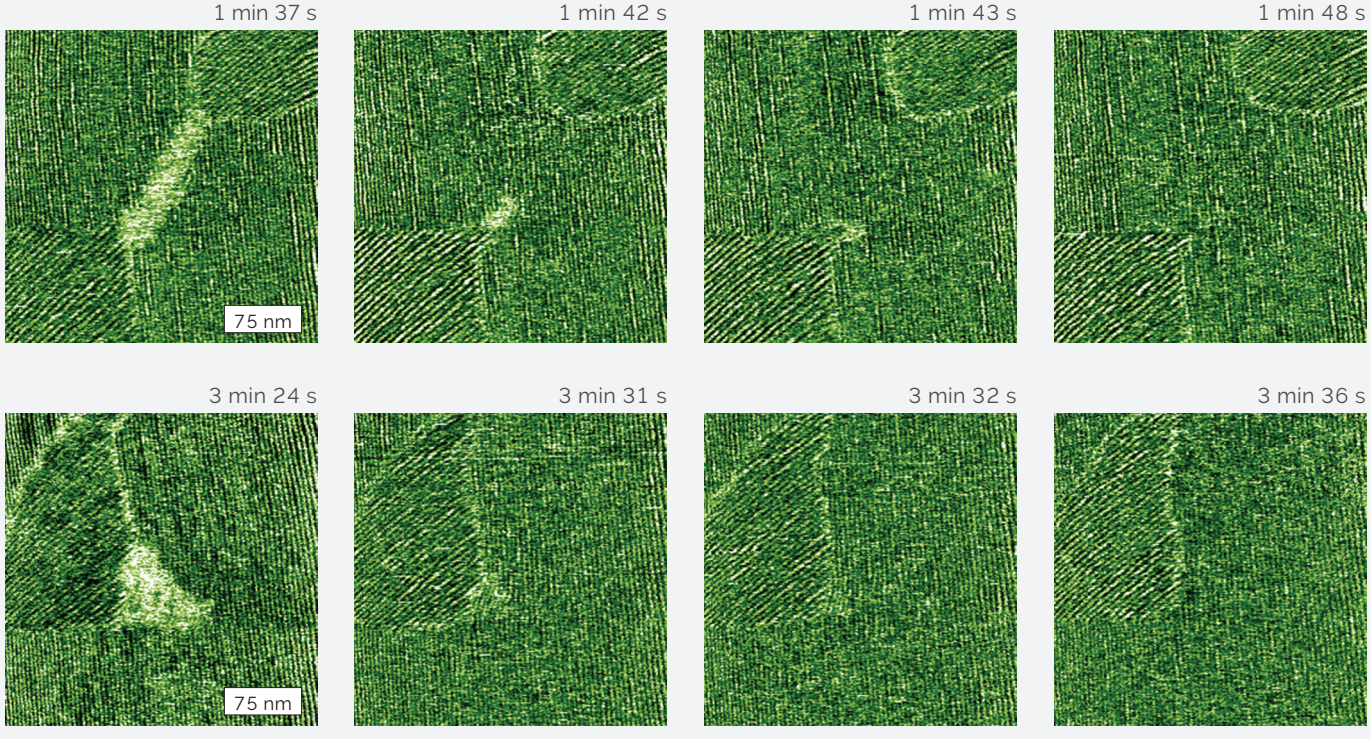

Figure 5: These two sequences of frames (top and bottom) were taken from a video acquired 0.95 fps (250 Hz line rate). Both examples show small features that seem to absorb into surrounding grains. The process appears analogous to Ostwald ripening, except in this two-dimensional system instead of a bulk dispersion. In both cases, the feature appears with higher phase contrast and appears less structured than the surrounding hemimicelles. The full video also shows how the scan size and offset can be adjusted during the video acquisition to survey a wider area. See it at: http://AFM.oxinst.com/CTAB

Conclusion

A wide range of dynamic events are now within the temporal resolution of video-rate AFM, including many biochemical reactions, self-assembly processes, and the non-equilibrium evolution of phase and grain structures. By combining high speed with high-resolution performance, the Cypher VRS video-rate AFM now makes it possible to visualize and quantify the dynamics of surfactant micelle behavior at solid-liquid interfaces. We anticipate that this capability will enable new research that will expand our theoretical understanding of surfactant self-assembly and the practical applied uses of these molecules.

References

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