

Imaging Cyanine Dye Aggregates on Silver Halide Emulsion Grains with Atomic Force Microscopy

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Abstract

Atomic and lateral force microscopy (AFM and LFM) have been utilized to characterize the macroscopic and microscopic surface structure of spectral sensitizing dye J-aggregates on gelatin-grown silver bromide tabular emulsion grains. The macroscopic J-aggregate morphologies and orientations are in excellent agreement with images obtained from both low-temperature photoluminescence microscopy and scanning electron microscopy (SEM). Further characterization of these J-aggregates are enhanced by the use of LFM that aids in distinguishing gelatin regions from dye aggregate regions on the tabular grain surface. Preliminary high-resolution AFM imaging failed to detect molecular structure. Energy minimization calculations indicated that sulfopropyl groups, appended to the thiacarbocyanine dye molecule for improved solubility, had a significant amount of dynamic motion resulting in a possible degradation of the AFM imaging mechanism. To improve the experimental imaging conditions for obtaining molecular resolution novel cyanine dye molecules without long-chain solubilizing groups were synthesized. In addition, rigid pendant groups such as biphenyl or t-butyl phenyl were added to benzimidazole cyanine dye molecules to aid molecular detection. These cyanine dye materials generated J-aggregates that yielded the first molecular resolution images of a J-aggregate region on gelatin-grown emulsion grain utilizing AFM.

Introduction

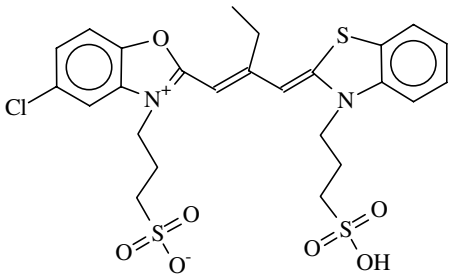
The practical application of silver halide photographic materials requires the adsorption of sensitizing dyes to extend their spectral sensitivity to longer wavelengths. When adsorbed to silver halide surfaces, these sensitizing dyes can form two-dimensional aggregates with narrowed and wavelength-shifted absorption envelopes. The physical structure of these aggregates and how they are related to the underlying silver halide surface have been active areas of research.[1-6]

In the last decade, a considerable amount of research has been reported on the application of scanned probed microscopies (SPM) and the structure of silver halide surfaces. Ever since Haefke et al. obtained the first atomically resolved images of AgBr{001},[7] there has been a great deal of interest concerning the confirmation of various proposed models for reconstructed {111} surfaces of silver bromide.[8] Several researchers have also pursued the utilization of both scanning tunneling microscopy (STM) and atomic force microscopy to study the structure of cyanine dye aggregates adsorbed to silver halide materials.[4-6,9] The combination of cathodoluminescence microscopy and AFM has been used to suggest three-dimensional aggregate structures on surfaces of cubic emulsion grains, but high-resolution imaging was not reported.[4] In addition, the unique identification of dye-aggregate regions from gelatin regions appeared challenging. Model surfaces, prepared in the absence of gelatin by either vacuum evaporation of silver bromide or chemical modification of Ag{111}, have facilitated atomic resolution of silver halide surfaces and molecular resolution of dye aggregates by STM.[5,6,10] Well-resolved STM images of the local structure of H- and J-aggregates have been correlated with optical absorption properties.[6] Although these model substrates provide a conductive substrate required for STM imaging, their lattice constants suffer from deviations from ideal values and cannot provide essential crystallographic information of the underlying silver halide host when dye aggregates are present.

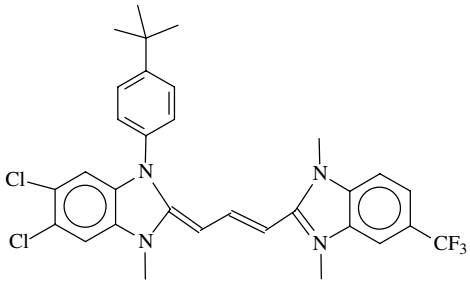
In this paper, the application of AFM imaging techniques to tabular emulsion grain surfaces with well-characterized J-aggregate regions will be discussed. Although AFM has lower resolution capabilities than STM, the advantage of this approach is reflected in the potential for characterizing both the J-aggregate structure, prepared under photographic conditions in the presence of gelatin, and the crystallography of the underlying host emulsion grain.

Experimental

The dyed silver halide material examined in this study has been previously described and characterized by low-temperature luminescence microscopy (LTLM).[3] Silver bromide tabular grains with equivalent circular diameters of 17 µm were precipitated in oxidized gelatin. **Dye I**, a benzoxazolobenzothiazolo carbocyanine dye (referred to as dye L in reference 3) has an absorbance maxima in methanol of 522 nm. J-aggregates of **Dye I** were prepared in a methanol environment at elevated temperatures referred to as the M method in reference 3. This method of spectral sensitization generated large 1-3 µm 'cigar'-shaped single-crystalline two-dimensional J-aggregates as characterized by polarized LTLM and SEM. The total dye quantity was calculated to cover approximately 50 percent of the tabular grain surface with a monolayer of dye. In addition, **Dye II**, a benzimidazole carbocyanine dye having both a pendant asymmetric tertiary butyl phenyl moiety and the elimination of sterically hindered solubilizing groups, was synthesized to facilitate improved molecular resolution imaging. **Dye II** has an absorbance maxima in methanol of 505 nm. J-aggregates of **Dye II** were similarly prepared utilizing the M method and characterized by LTLM. While LTLM revealed luminescent J-aggregate regions, clearly identifiable morphological structures were not observed.



Dye I



Dye II

A commercially available instrument was utilized for AFM and LFM.[11] Vibration isolation and operation in an anechoic facility improved signal quality. Monolithic silicon tips having tip radii measured to be ~20 nm and experimentally determined force constants of ~0.3 N/m and resonance frequencies of ~25 kHz were utilized for imaging most samples. Contact forces were maintained near 1 nN.

Excess gelatin was removed from emulsion samples by digestion with an enzyme solution at both room temperature and 40 °C followed by rinsing with distilled water. The washed emulsion was placed on cleaved mica and excess liquid wicked away. The dye was confirmed to be present after AFM sample preparation by re-examination of dye aggregate luminescence. All sample preparation and AFM imaging was done under red safe-light conditions.

Results and Discussion

Identifying Large J-Aggregate Features with AFM

Figure 1 is a 5 µm x 5 µm AFM topographic image of a portion of a AgBr tabular emulsion grain having J-aggregates of **Dye I**. The grain edge is on the left-hand side of the image and provides an internal crystallographic reference parallel to the <110> direction. The image contrast has been optimized to only highlight features in the near-surface region and not the entire tabular grain's thickness. Large 'cigar'-shaped J-aggregate regions are clearly observed and their orientations and morphologies are in excellent agreement with previously reported LTLM observations.[3] Based on several images of different tabular grains approximately half of the surfaces are covered with dye aggregates. This is consistent with the calculated surface coverage of a single monolayer of dye and not a three-dimensional aggregate. These large J-aggregates vary in size from one to three microns in length and have widths of approximately one micron or less. AFM also provides highly accurate measurements of the orientations of these aggregates, 20 ± 2°, with respect to the <110> direction of

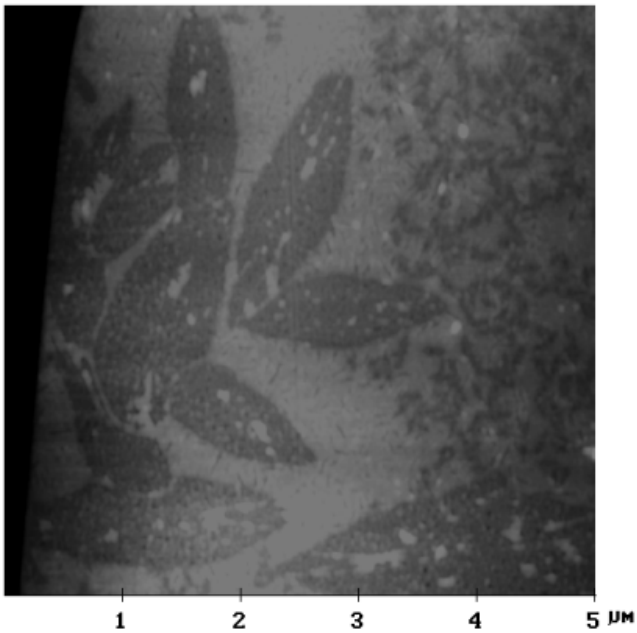


Figure 1. AFM image of **Dye I** *aggregates on AgBr tabular grain.*

the AgBr host surface that confirm a characteristic angle for **Dye I** of 20° found with polarization studies using LTLM.

In addition to the macroscopic orientation and morphology the relative topography of these aggregates is intriguing. With excess gelatin removed it was anticipated that dye-aggregate regions would extend *above* the nominal silver halide surface with approximately molecular dimensions of less than a nm. However, all aggregate regions imaged have been observed as apparent depressions into the nominal tabular grain surface. The sample prepared for Fig. 1 used an elevated temperature enzyme treatment and the apparent aggregate depth varies between 1 and 3 nm. This sample also showed some indication of printout degradation. The existence of topographically depressed regions associated with the J-aggregates suggests two hypotheses. (i) A significant amount of residual gelatin remains adsorbed to the silver halide region, and/or (ii) the high temperature and solvent environment used to form these large aggregates has ripened silver halide material and grow the thickness of the tabular grain in regions not occupied by the J-aggregates.

The spatial resolution of the AFM also reveals additional detail not resolvable by the optical microscope used in the luminescence study. In the right-hand portion of Fig. 1 a large number of significantly smaller regions are identified. Based on their exact orientation, morphology and depth it is suggested that these depressions are smaller J-aggregates approximately 100 nm in length.

Molecular Resolution with AFM

One goal of this work is the imaging of an aggregate structure with molecular resolution and ultimately identifying the underlying relationship between a dye's orientation and the silver halide lattice. Figure 2 is a 1 μm x 1 μm topographic region of a single 3 μm-long 'cigar'-shaped J-aggregate of **Dye I**. The curving perimeter of the 'cigar' aggregate is located at the top of the image in Fig. 2. This sample was prepared with a gentler room temperature enzymatic digestion and exhibits significantly less degradation from printout. Associated with this preparation condition, a greater amount of residual gelatin remains and actually covers some portions of the large J-aggregate in this image. The height of the gelatin above the aggregate surface is ~5-10 nm in Fig. 2. Unlike the sample prepared for Fig. 1, the aggregate region in Fig. 2 showed very little topographic variability (±0.1 nm). However, extensive high-resolution imaging on an aggregate region did not yield reproducible molecularly resolved images. Molecular dynamics and energy minimization calculations of **Dye I** suggested one possible explanation for the poor quality of the high-resolution images. The sulfo-propyl groups, which are oriented away from the silver halide surface and toward the AFM stylus, showed a tendency for a high degree of motion. It is possible that during raster scanning motion of the AFM tip the sulfo-propyl groups may move and obstruct ideal imaging conditions.

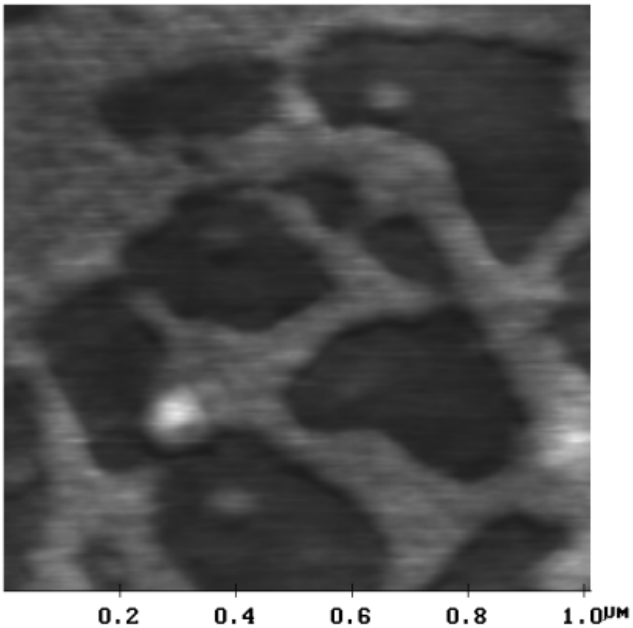


Figure 2. AFM image of 'cigar'-shaped aggregate of **Dye I**.

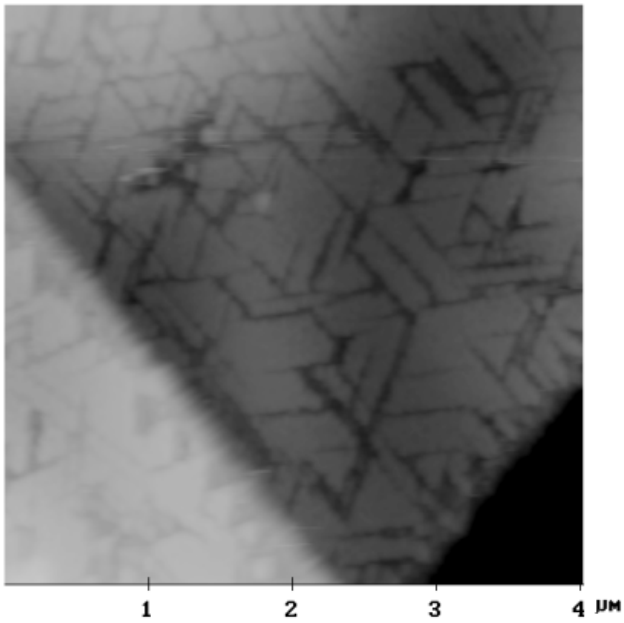


Figure 3. AFM image of two overlapping AgBr tabular grains having rod-shaped aggregates of **Dye II**.

Dye II was synthesized to provide an improved opportunity for molecularly resolved imaging of a dye aggregate. The elimination of the sulfo-propyl groups and the addition of a phenyl moiety with a bulky tertiary butyl group were hoped to enhance the ability for AFM to detect molecular structure. Figure 3 is a 4 μm x 4 μm topographic image of two overlapping tabular grains having aggregates of **Dye II**. Unlike the 'cigar'-shaped morphology of **Dye I**, **Dye II** appears as 'rod'-shaped segments rarely over a

micron in length. 'Rods' intersect with well-defined 60 or 120 degree angles and appear as 15-20 nm depressions into the nominal surface. The orientation of the rods is reminiscent of the threefold symmetry of the underlying silver bromide {111} structure, but it is important to note that the long dimension of the aggregate structure has an ~11° offset from ideal commensurability. Figure 4 is a ~900 nm x ~900 nm detailed image of J-aggregate

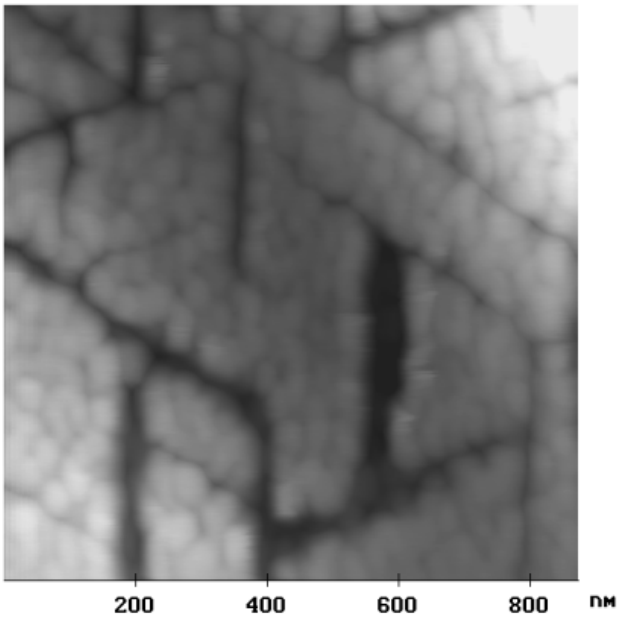


Figure 4. AFM image of Dye II rod-shaped aggregates.

orientations of **Dye II**. Figure 5 is a high-resolution 8.5 nm x 8.5 nm image within the larger aggregate region (400 nm x 40 nm) near the center of Fig. 4. Image processing has

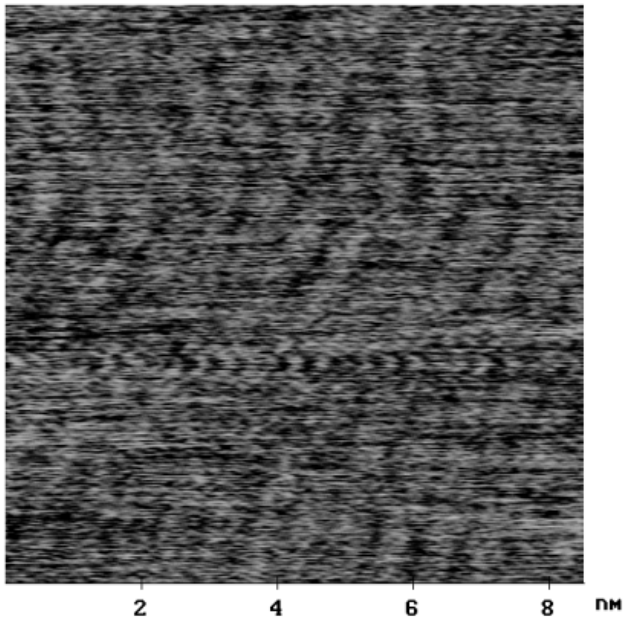


Figure 5. High-resolution topograph of **Dye II** *aggregate region.*

been used to enhance the images' features, but a weak herringbone-stacking pattern can be observed in the original image. The lower resolution capabilities of AFM versus those of STM make precise assignment of the molecular structure difficult. Assuming correct identification of **Dye II** molecules in the aggregate region of Fig. 5, it is suggested here that the long axis of the molecule is aligned 15 ± 4 degrees with respect to the <110> AgBr lattice direction. Improving the resolution capabilities of AFM and increasing both the number and type of cyanine dyes examined will aid in identifying structural properties related to the chemisorption and/or physisorption of aggregates.

Identifying Large J-Aggregate Features with LFM

One of the clear challenges for many scanned probed microscopy (SPM) techniques is the confident identification and characterization of meso-scaled features. Clearly in the example presented in this work, the presence of previously characterized and easily recognizable morphologies (i.e., 'cigar'-shaped) aided in the identification of the large J-aggregates. Interpretations of different chemical regions, such as those on an emulsion grain, based solely on topographical differences, in the absence of clear morphological 'fingerprints', can lead to misinterpretation of emulsion grain regions that may be covered with gelatin, ripened silver halide, or dye aggregate. The use of lateral force microscopy, LFM, was examined as a possible tool to improve identification of chemically distinct regions. LFM utilizes the torsional signals and not the vertical displacement signals of the AFM cantilever and tip to record differences in 'so-called' frictional forces as the tip encounters differing chemical interactions along the raster scanned direction.. Figures 6 and 7 are simultaneously

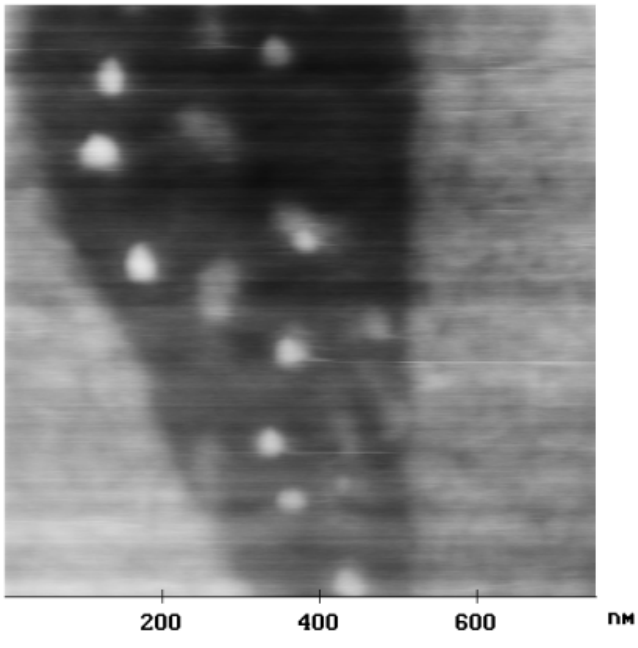


Figure 6. AFM image of Dye I *simultaneously obtained as Fig. 7.*

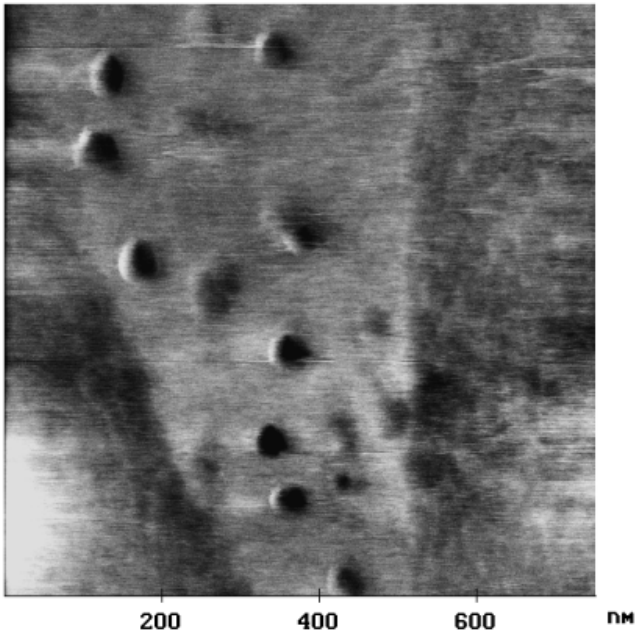


Figure 7. LFM torsional image of **Dye I** *identical to Fig. 6.*

acquired 800 nm x 800 nm topographic and torsional images respectively of a 'cigar'-shaped J-aggregate region of Dye I. The sample had been intentionally exposed to ambient light to induce some degree of photolysis. The large white specks in the topographic region, heights of 10-20 nm, are interpreted to be silver metal printout within the aggregate region. While the topographic image shows the expected height differences for the gelatin and aggregate regions, ~9 nm, the torsional image shows that the dye aggregate region has a different interaction with the tip than the gelatin region. The magnitude of the torsional signals within the aggregate region suggests that there is a stronger interaction between the tip and **Dye I** than the tip and residual gelatin. For the emulsion grain system, it is not known if these torsional signals are associated with an electrostatic or chemical interaction. Similarly, the structures thought to be printout show essentially no interaction with the tip—consistent with a non-interacting metal surface.

Conclusions

AFM and LFM imaging of large J-aggregates have confirmed expected morphological structures originally observed with luminescence microscopy. The usefulness of LFM was explored as a possible method for improving the identification of different chemical regions without the aid of distinct morphological structures. In addition, preliminary high-resolution imaging has attempted to relate molecular orientation of dyes to the silver bromide host lattice structure.

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8. See, e.g.: H. Nozoye and H. Takada, *Jpn. J. Appl. Phys* **33**, 3764 (1994); *Langmuir* 9, 3305 (1993).
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Biography

Jeffrey Hansen received his B.A. degree in Chemistry from Gustavus Adolphus College in St. Peter, MN in 1983 and a Ph.D. in Chemistry majoring in materials science from the University of Wisconsin-Madison in 1989. Since 1989 he has worked in Eastman Kodak Research Laboratories in Rochester, NY. His work has focused on the electronic properties and geometrical structures associated with surfaces and interfaces of silver halide emulsion materials.