

Atomic Force Microscopy of an Organic Adsorbate on the Surface of Silver Halide Crystals

Katsuhiko Suzuki

Konica Corporation, Tokyo, Japan

Hisakazu Nozoye

National Institute of Materials and Chemical Research

Tsukuba, Ibaraki, Japan

Abstract

In order to explore the usefulness of atomic force microscopy (AFM) in the analysis of silver halide photographic systems, molecular AFM images of an organic adsorbate on silver halide were obtained. A sensitizing dye, 2,2'-cyanine, adsorbate on single grain films of AgBr cubic crystals were examined and a molecular image was clearly observed.

It was revealed that 2,2'-cyanine had a two dimensional arrangement of $a=0.8(\text{nm})$, $b=1.6(\text{nm})$, and $\beta=118\sim 130(\text{deg})$, with approximately 10 degrees of slip angle from the AgBr $\langle 010 \rangle$ direction, suggesting a model of adsorption.

Introduction

In silver halide photographic systems, organic adsorbates on the surfaces of silver halide crystals, such as sensitizing dyes and restrainers, have important roles in the photo-sensitizing process. Many studies of the adsorbed states of organic adsorbates have been reported, but few include image observations of the adsorbate because of the susceptibility of silver halide crystals to damage from analyzing probe such as light, electron beams, and X-rays.

Maskasky¹⁾ reported J-aggregate observations using low-temperature luminescence microscopy, and Saijo et al. reported J-aggregate observation using color fluorescence electron microscopy²⁾ and scanning electron microscopy³⁾. These very important studies present direct observations of the J-aggregates of sensitizing dyes on silver halide microcrystals. But in these studies, the images of adsorbates obtained were not on a molecular level.

Recently, such typical forms of SPM(scanning probe microscopy), as AFM and STM(scanning tunneling microscopy), have been widely used for atomic- or molecular-level imaging, including the direct observation of adsorbates on solid surfaces. While STM, with its need for electric conductivity, has limited applicability to silver halide study (except in such isolated cases as when samples form thin layers), AFM promises wide application to atomic and molecular scale observation in silver halide photographic systems.

Some silver halide crystal studies using AFM, such as

bulk crystal surface observations^{4,5)} and evaporated surface observations⁶⁻⁹⁾ have been reported. Takada and Nozoye obtained atomic images of the surfaces of silver halide microcrystals, and suggested the usefulness of AFM as a method of imaging silver halide photographic systems on an atomic level¹⁰⁾. Kawasaki et al. reported obtaining molecular-level STM images of sensitizing-dyes on carbon graphite surfaces¹¹⁾ and metallic silver surfaces¹²⁾.

The object of this study was to explore the usefulness of AFM in the analysis of silver halide photographic systems by studying molecular AFM images of an organic adsorbate on the surface of silver halide microcrystals. AFM, and especially contact AFM, is generally used in the study of organic molecule imaging on solid surfaces, and if practical in the study of silver halide crystals, AFM would offer several advantages:

1. High resolving power allows atomic- or molecular-level observation.
2. Specific areas on a molecular scale can be selected for observation.
3. No probe radiation is present to damage silver halide crystals.
4. No electric conductivity requirements are made of samples.
5. No specific atmosphere such as a high vacuum is needed.

Naturally, potential problem with AFM had to be dealt with. One such potential problem was possible damage to samples by the tip. When observing weakly adsorbed substances such as organic adsorbates on silver halide microcrystals, it is important to minimize the forces exerted between the tip and the sample surface. In contact AFM, these forces of attraction and repulsion may be in balance and thus may not be reflected by any flexure of the cantilever. The forces, however, are none-the-less present, and can deform the adsorbates and/or remove them from the sample surface. To minimize these forces and maintain stable observation, it is necessary to reduce interaction between the tip and sample. One way of doing this is conduct the AFM observation in water, a method widely used in the imaging of organic adsorbates on solid surfaces^{13,14)}.

Another potential problem with AFM was that when silver halide microcrystals are being observed, the tip can

sometimes move the crystal grains as it travels over the grains, preventing observation. This can be avoided, however, by preparing the samples consisting of a single film of closely packed crystals, as Takada and Nozoye reported¹⁰⁾

Therefore, in our study, sample damage was minimized by conducting AFM observation in water, and micro-crystal movement was prevented using single grain film samples.

Experimental

Sample preparation

Following Heki¹⁵⁾, closely packed single grain films of AgBr cubic crystals were prepared. The AgBr emulsions were thoroughly washed with water. The emulsions were then diluted in water, and the water stirred or agitated with bubbling air. The crystals brought to the water's surface were then picked up on to an ITO (Indium Tin Oxide) substrate (6.0mm x 5.0mm) which was dipped in the water. In this way, closely-packed, single grain film samples of AgBr cubic crystals (edge length about 1.0 μ m) were fabricated (Fig. 1).

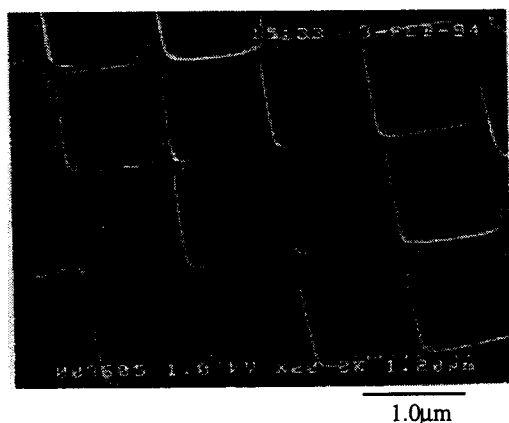


Fig.1 Scanning electron micrograph of a single layer of cubic AgBr grains.

Cyanine sensitizing dye solutions were prepared consisting of 0.03% 1-ethyl-2-[(1-ethyl-2(1H)-quinolinylidene)methyl]quinolinium bromide (2,2'-cyanine) solution (H₂O:methanol=1:1) diluted with 20 parts water, and 0.045ml of this diluted solution were applied in droplet form to each film sample. After storing at room temperature for 30 minutes, the film samples were rinsed with water. Structure of 2,2'-cyanine is shown in Fig.2.

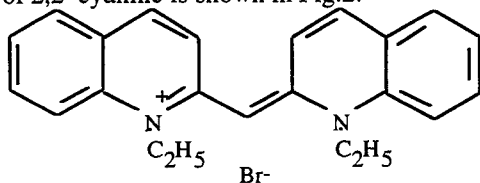


Fig. 2 Structure of 2,2'-cyanine.

AFM observation

Constant force mode AFM observation was carried out in water using NanoscopeII (Digital Instrument) AFM system, a commercially available Si₃N₄ cantilever (spring constant

0.38N/m) and an A-scanner (maximum observation area 0.7mm square). The samples were stored in water following Drake et al.¹⁵⁾. A transparent plate was attached with a cantilever mount, and the water was held between transparent plate and sample holder by surface tension. During observation, force curves were measured periodically and adjustments were made to minimize the forces acting on the sample surfaces. The images obtained were digitally processed for flattening and contrast control.

Results and Discussion

Fig.3 shows an AgBr (001) surface without adsorbate. The bright spots indicate surface protrusions of, as Takada and Nozoye reported¹⁰⁾, either Ag or Br, but probably Br, since Br has a larger ionic radius. The arrows indicate the orientation of the AgBr crystal lattice, which was determined from macroscopic observation of crystal grains.

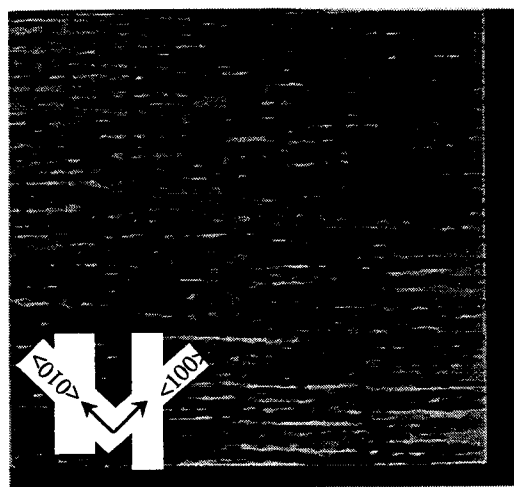


Fig. 3 AFM image of the AgBr (001) surface without adsorbate (10nm x 10nm).

Figs. 4(a) and (b) are of AgBr (001) grains with 2,2'-cyanine adsorbed on their surfaces. Fig. 4(b) is of the same surface as Fig. 4(a), but at higher magnification. Along side the AFM image in Fig. 4(b), a molecular model of 2,2'-cyanine is presented in scale. That these images are of the adsorbate is indicated by their periodicity and symmetry, which differ from those in the image of AgBr (001) surface without an adsorbate seen in Fig. 3. The size of the bright spots in the Fig. 4 images matches the 2,2'-cyanine molecule size very well, and the two quinoline rings connected by monomethine chain can be clearly observed. Dammeier and Hoppe report determining from single crystal structure analysis that the planes of two quinoline rings of 2,2'-cyanine are tilted from each other at a 50.6-degree angle¹⁶⁾. In the adsorbed state, the rings can be expected to be similarly tilted, and this is consistent with the AFM images seen here.

The periodicity and symmetry of these AFM images and their relation to the AgBr crystal orientation suggests

the 2,2'-cyanine molecular arrangement model shown in Fig.5. In this model, the dark dots represent Ag or Br lattice points. This model has a two-dimensional arrangement of $a=0.82(\text{nm})$, $b=1.47(\text{nm})$, and $\beta=123.7(\text{deg})$, and $\theta=11.3(\text{deg})$, the slip angle from the AgBr $\langle 010 \rangle$ direction. In comparison, our observed values are $a=0.8(\text{nm})$, $b=1.6(\text{nm})$, $\beta=118\sim 130(\text{deg})$, and $\theta=10(\text{deg})$, which closely approximate the model.

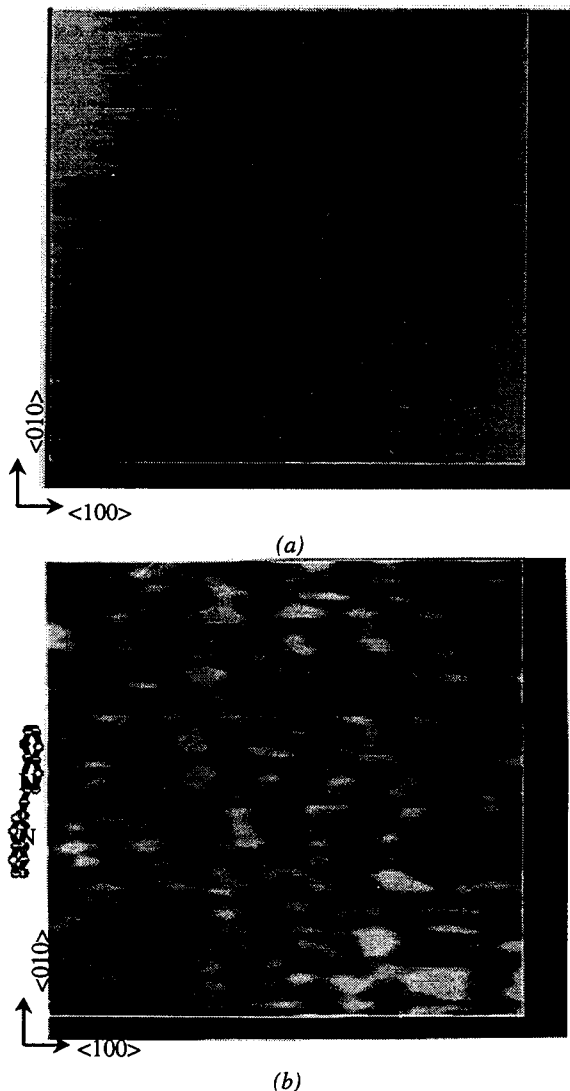


Fig.4 AFM images of AgBr (001) grains with 2,2'-cyanine adsorbed on their surfaces. (a) 10nm x 10nm (b) 4nm x 4nm

In this study, we do not deal with the relation between the AgBr lattice and the adsorbate arrangement, except for the slip angle. But assuming that the adsorption sites of 2,2'-cyanine are the two N atoms, proposed model appears reasonable because the distance N-N closely approximates the lattice point spacing (0.58nm) of the model.

The adsorption pattern proposed by the model is similar to the staircase arrangement of J-aggregates reported by Scheibe et al.¹⁷⁾ and Smith¹⁸⁾. Macro observation of the samples in our study showed no islands caused by multilayer adsorption, indicating that the adsorption pattern

here reflects strong, single-layer adsorption, with the crystal surfaces and adsorbates closely and commensurately related.

Maskasky¹⁾ reports that the orientation of J-aggregates of 2,2'-cyanine on AgBr(001) surfaces corresponds to $\langle 110 \rangle$ direction of the crystal. But he also states that this orientation of J-aggregates does not directly indicate molecular orientation. In our study, it was shown that one axis of the two-dimensional lattice of the adsorption layer corresponds to $\langle 110 \rangle$ direction, though the relationship between the orientation of the J-aggregate and the molecular orientations of the adsorbate was not obtained. However, it appears possible to use AFM to observe the orientation of the J-aggregate and the molecular orientations of the adsorbate in the same sample crystal, and this is one of many promising AFM applications worthy of study in the future.

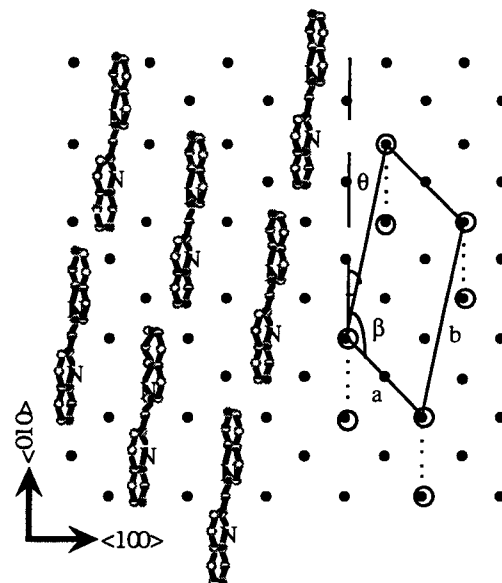


Fig.5 Proposed adsorption model for 2,2'-cyanine on the AgBr (001) surface.

Conclusion

Takada and Nozoye, along with others, have shown the possibility of using AFM for atomic- and molecular-level imaging of silver halide photographic systems. In this study, AFM was used on this scale to produce images of sensitizing dyes on silver halide microcrystals. Only one kind of organic adsorbate was observed in this study. But with such recent progress as the widening of applications through the use of tapping mode and the increase of resolving power through the use of acute tips, AFM promises to play an increasingly important role in the analysis of silver halide photographic systems, including dynamic processes.

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