Atomic Force Microscopy Observation of Cyanine Dye J-Aggregates on AgBr Microcrystals Grown in Gelatin

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The morphology of thiacarbocyanine and oxacarbocyanine dye J-aggregates adsorbed on (001) surfaces of AgBr microcrystals grown in gelatin was observed by atomic force microscopy. No residue of fibrous gelatin was found on the specimen. The cyanine dyes grew in islands or stripes by means of the Volmer–Weber growth mode, rather than by monolayer adsorption. The thickness of stripes varied from 0.5 nm (monolayer) to 30 nm, and the stripes were constructed of many rectangles [20 × (35–50) nm]. The rectangles were regarded as elementary crystallites or J-aggregate particles photoelectrically separated from one another.

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Introduction

The photographic process begins when photons are absorbed by the cyanine dye J-aggregates adsorbed on silver halide microparticles. The morphology and structure of the aggregates on silver halides grown in gelatin were, however, not revealed by any microscopic methods before the work that we recently reported.[1–5]

Analytical color fluorescence electron microscopy (ACFEM) was used in our first study to observe quinocyanine (1,1'-diethyl-2,2'-cyanine iodide) and an oxacarbocyanine (3,3'-bissulfopropyl-5,6,5',6'-dibenzo-9-ethyl-oxacarbocyanine triethyl ammonium salt) dyes on AgBr microcrystals, and we succeeded in visualizing their J-aggregates as green and/or red cathodoluminescent spots.[1] The aggregates were about 30 × 70 nm, aligned along the <110> or <210> directions on the (001) surfaces of AgBr. A color change of the luminescence spots from yellowish green to orange red was observed in ACFEM images of the oxacarbocyanine.[2] The change was ascribed to a change of energy state due to the release of secondary electrons by electron irradiation. The inverse color change, which was also observed in the same image, can be regarded as a recovery process of the dye.

We also used the ACFEM process to study the nucleation and growth mechanism of J-aggregates on the surface.[3] The J-aggregates nucleated when dye molecules were added to the gelatin sol of AgBr microcrystals. Residual dyes in solution after the nucleation worked only to increase the sizes of existing aggregate nuclei on the surface, and the dissolved dyes did not contribute to forming the nucleus of a new aggregate. In the same study, we also discussed temperature effects during aging on the size of J-aggregates and the surface selectivity for adsorption. The luminescence color (wavelength) of oxacarbocyanine J-aggregates showed a close correlation with their sizes, which means that the luminescence color becomes a good measure of aggregate size with adsorption.

Next we tried direct observation of J-aggregates with a room-temperature ultra-low-energy scanning electron microscope (SEM).[4] Thiacarbocyanine (3,3'-bissulfopropyl-5,5'-dichloro-9-ethyl-thiacarbocyanine sodium salt) dye J-aggregates nucleated epitaxially on the (001) AgBr surface, and they grew in stripes along the [210] and/or [120] direction. We then postulated that the stripes were constructed with photoelectrically separated J-aggregate particles, taking into account ACFEM results.[5] We also found that the electron irradiation sprouted Ag filaments preferentially on the area that the oxacarbocyanine J-aggregates covered on the (001) AgBr surface.[6]

The morphology and topography of J-aggregates adsorbed on silver halide microcrystals might best be depicted by scanning force microscopies. Haefke et al.,[7] in an illustration of the powerful utility of atomic force microscopy (AFM) for obtaining information about the beam-sensitive surfaces of AgBr photographic systems, showed an AFM image of a merocyanine dye film on a vacuum-deposited AgBr thin film. The vapor-deposited merocyanine film with a nominal thickness of 3 nm grew in the form of three-dimensional islands, rather than in layers by the Frank–Van der Merwe growth mode. The heights for rod-shaped islands were between 40 and 80 nm and the rounded-shape island height reached as much as 100–300 nm. They noted that this result was in contrast to conventional wet sensitization results.

Our present study correlates our recent AFM observations of the dye J-aggregates on AgBr with the morphological structures mentioned earlier. The thickness of a one-unit dye layer is estimated from the analysis of vertical data for J-aggregate islands.

Experimental

The emulsion crystals were prepared in the same way as those prepared in our previous studies.[1–6] AgBr cubic crystals of 0.7 μm edge length were grown in gelatin, and then thiacarbocyanine dye or oxacarbocyanine dye was added to cover their surfaces at S = 10 or 40%, where S is the nominal coverage at which the dye is entirely adsorbed on the {001} AgBr surfaces as a monolayer. We also prepared blank specimens without dye adsorption. The microcrystals were arranged two dimensionally in a monolayer and rid of gelatin by a special method reported by Heki and Inoue.[8] In this method, gelatin is removed by means of repeated dilution with warm water and decantation, and no enzyme treatment was employed to fragment gelatin.

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The (001) AgBr surfaces with cyanine were directly observed in contact static mode AFM with a scanning probe microscope (TopoMetrix TMX-2000) at the Scientific Instruments Center, Nissei Sangyo Co. The movement of the probe is detected with 670-nm laser light. Because the thiacarbocyanine dye J-aggregates absorb at about 580 nm[9] and the oxacarbocyanine at 550 nm,[1] the laser light hardly exposes the specimen. The present system can draw two surface topography maps, using either left-to-right or right-to-left probe movements in one frame scan. We checked artificial surface modification by the probe movement by comparing these two topographic maps and thus verified the surface features of the image. The measurements were carried out at room temperature in ambient air.

Results and Discussion

Figure 1 shows AFM images of AgBr microcrystals without adsorbed dye. Two-dimensional distribution of the 0.7-μm cubic particles is reproduced in Fig. 1(a). Though the surface contains some small undulations of less than 1 nm in height, the fibrous bodies that were observed in a previous study[10] could not be found in the image. We concluded that gelatin did not remain on the surface of AgBr prepared by the method described in Ref. 8.

An AFM image of the AgBr surface with thiacarbocyanine dye J-aggregates is shown in Fig. 2(a). The quantity of dye molecules is as much as will cover S = 10% of the crystal surface in a monolayer. Stripes on the surfaces can be ascribed to J-aggregates, because we have observed similar images by SEM[4,5] and confirmed them by ACFEM.[1–3] The AFM image shown in Fig. 2(a) discloses the island formation of J-aggregates. Though the surrounding edge of the (001) surface suffered some scratches as a result of the probe hitting the side of the particle, no deformation was ascertained for the structures in the central part of the (001) surface, as ascertained by the double imaging method described in the experimental section.

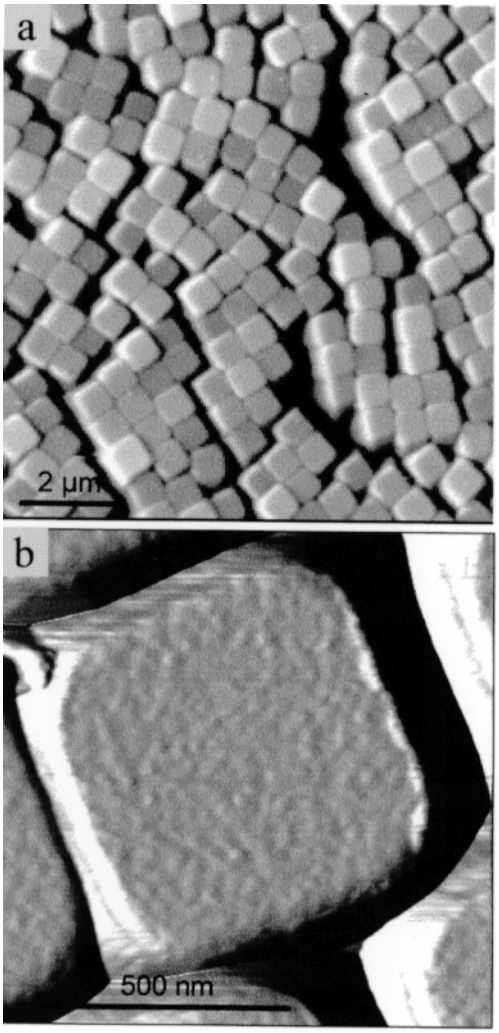


Figure 1. AFM images of cubic AgBr emulsion crystals on which no photosensitive dye is adsorbed.

Vertical analysis data along the X–Y line in Fig. 2(a) is shown in Fig. 2(b). Because the shape of vertical data is a convolution of the specimen profile and the outline of the probe tip, the shape always appears to vary more at the bottom of the curve than would the true trace of the specimen surface. Because the corresponding areas B, D, F, H, and J look flat in the image, we assume that they are at the surface level of the AgBr, z = 0. The crystal surface is not horizontal and the X–Y line has a gradient of 11/1000. Thus, A and C are positioned at z = 6.3 nm, E, G, I, and K at z = 8.4 nm, and L at z = 2.1 nm. These measurements led to the conclusion that the stripes or islands grew with thicknesses of at least 6.3 or 8.4 nm and with widths of several tens of nanometers. We should hence emphasize that the J-aggregates form in islands by the Volmer–Weber growth mode, rather than by monolayer adsorption. The thicknesses of 6.3 and 8.4 nm are three and four times 2.1 nm, and we consider the 2.1 nm to be the unit thickness of the thiacarbocyanine J-aggregates. The area near L seems to be covered with this unit layer.

Figure 3(a) shows an AFM image of thiacarbocyanine at S = 40%. The vertical data in Fig. 3(b) reveal that here the dye also grew in stripes of the thickness of 2.1n nm or n unit layers (n = 1–4). With increased coverage, the stripes became wider and united with each other.

The thiacarbocyanine dye is about $20 \times 10 \times 5$ Å, as calculated from the molecular structure, and the dye adsorbs edge-on.[11] We consider that the unit layer, 2.1 nm thick, contains two dye monolayers with their counter ions. This thickness, 2.1 nm, agrees well with the unit cell thickness of thiacarbocyanine J-aggregates with p-toluene sulfonic acid counter ions grown in solution and studied by x-ray crystallographic analysis.[12] The counter ions must occupy positions in the layer between the two dye layers.

An example of images of oxacarbocyanine at S = 10% is shown in Fig. 4, with a vertical data curve. The island structure is also seen. Two parts bounded by a [120]-stripe exhibit different contrast. If we assume the AgBr surface level to be at z in Fig. 4(b), then the thickness of stripes, for instance, is determined to be 9 nm for A, 17.5 nm for F, G, and H, and 28 nm for J. The lower contrast of peaks A–E comes from an underlying dye layer of thickness z' = 4.4 nm. The presence of the underlying layer and the unity of D with E (and of I with J) indicate a growth process from island to continuous film, although they are very natural for the thin-film growth.

In an image of the oxacarbocyanine at S = 40%, shown in Fig. 5, stripes as thin as 0.5 nm were found, along with 1-, 1.5-, and 2.5-nm-thick stripes. Because the height of the oxacarbocyanine dye molecule is estimated to be 0.5 nm from the x-ray structure analysis data for the thiacarbocyanine,[12] the stripes 0.5 nm thick are most likely monolayer dye and the others are multilayered stacks. The counter ions do not form separate layers intercalated between the dye monolayers, but should be included inside the dye layers.

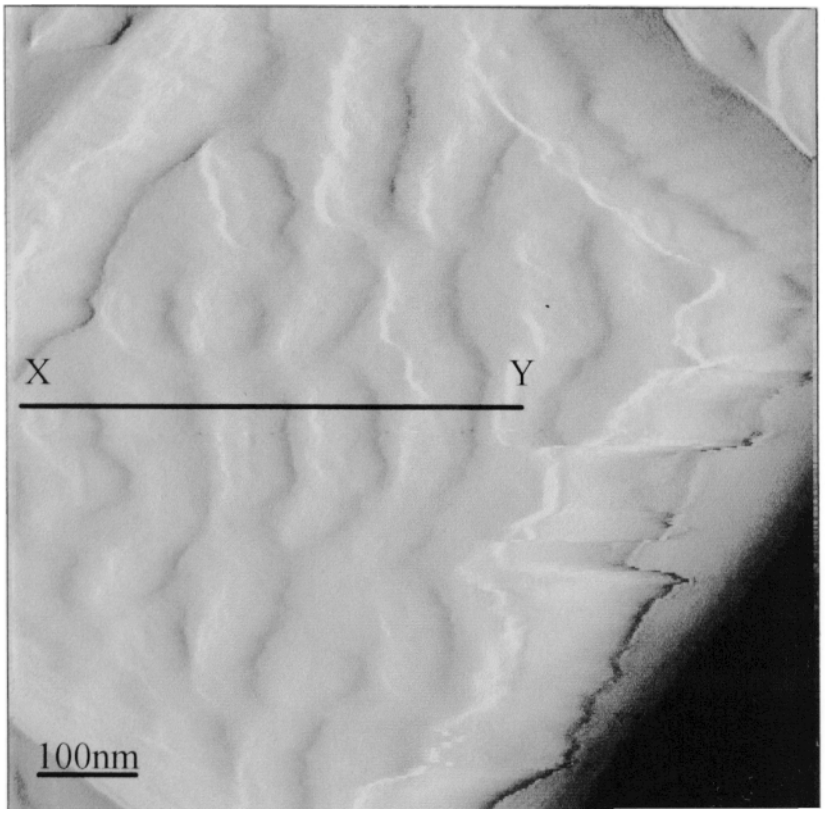
In earlier studies, we observed separated cathodoluminescence (CL) spots, a few tens of nanometers wide, in ACFEM images of this dye.[1–3] Some of the spots were

elongated along the <210> direction of AgBr, but no continuous bright line was seen in luminescence images. Each of the spots can be regarded as a single J-aggregate particle because of the CL spectra corresponding to the J-absorption band.[1] In the paper that dealt with SEM observations,[4] we assumed that the dye stripe was not a perfect single crystal but was composed of many parts like wagons in a train or elements in a mosaic. Each part is photoelectrically separate so that it works as a single J-aggregate particle. Fringes running obliquely through the stripes can be seen in the thicker area in Fig. 5(a). Figure 6(a) shows another image of the oxacarbocyanine. There we can see the stripes divided into small rectangles, which look like obliquely stacked match boxes, as shown schematically in Fig. 6(b). The sizes of the rectangles are about 20 × (35–50) nm. Each of them may be regarded as an elementary crystallite or J-aggregate particle, as discussed above.

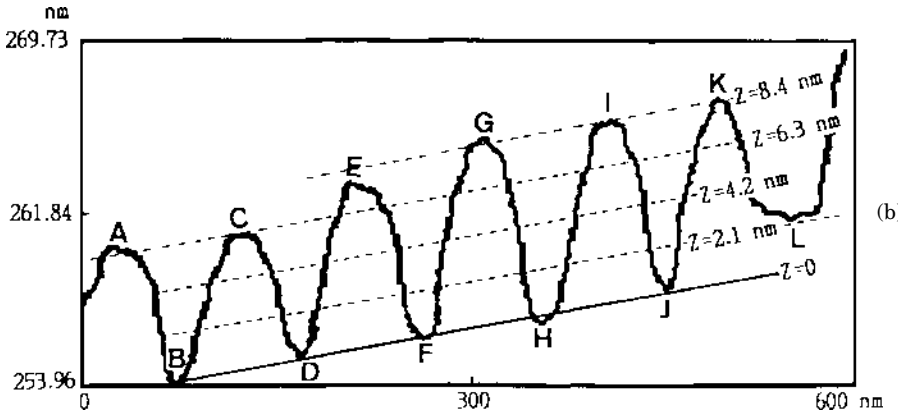
Thus it becomes clear that the J-aggregates do not always adsorb in monolayers but may also form thicker stripes in an island growth mode. The present specimens were prepared by repeated warm-water dilution and decantation to remove gelatin,[8] excluding condensing processes that is used in the enzyme treatment and centrifugal separation. We therefore believe that the AgBr surfaces observed in this study keep the conformation of the practical emulsion crystallite surfaces. We venture that the island growth of photosensitive dyes is not a special case in merocyanine dye films, as found by Haefke et al.,[7] but generally takes place in practical sensitizing dyes.

Conclusion

The (001) surfaces of emulsion cubic AgBr crystals having thiacarbocyanine or oxacarbocyanine dye at different coverages were observed by contact static mode atomic force microscopy. We found that the cyanine dyes grew in islands or stripes by the Volmer–Weber growth mode,[13] rather than by monolayer adsorption. The observed thicknesses of stripes varied from 0.5 nm (monolayer) to 30 nm. The stripes were constructed of many rectangles, which were arranged as shown in Fig. 6(b). The rectangles were regarded as elementary crystallites or J-aggregate particles photoelectrically separate from one another.



(a)



(b)

Figure 2. (a) AFM image of thiacarbocyanine J-aggregates at $S = 10\%$ on (001) AgBr microcrystal. (b) Vertical data along line *X*–*Y* in (a).

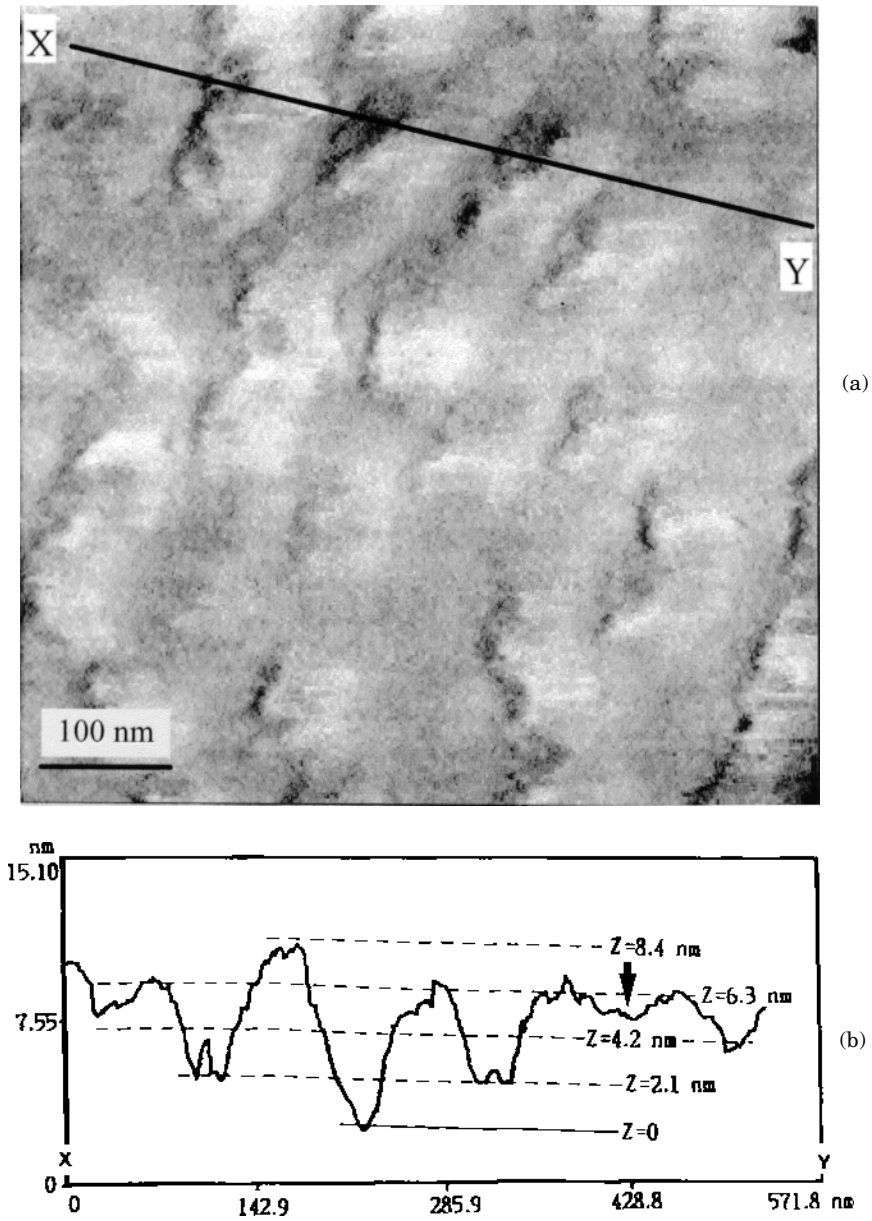
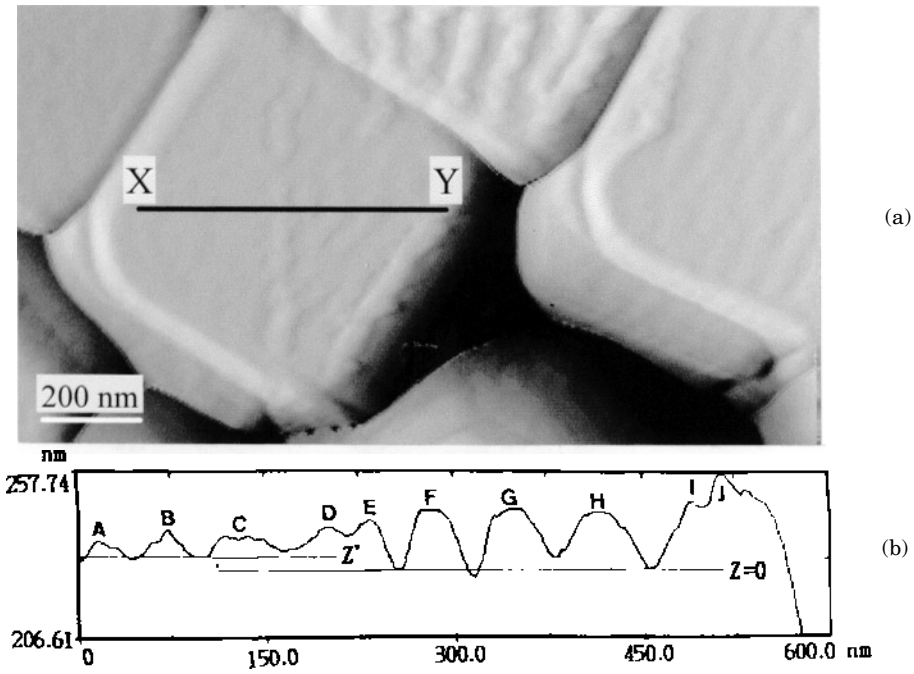


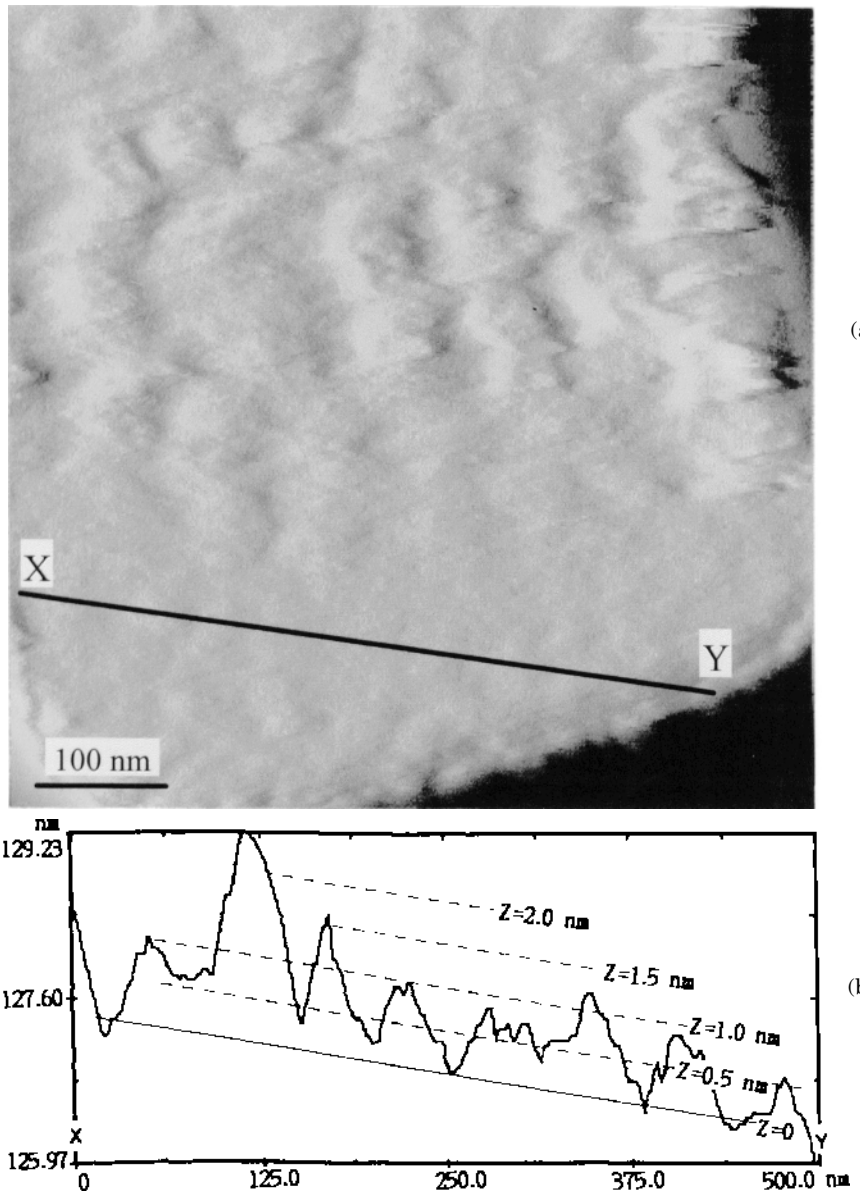
Figure 3. (a) AFM image of thiacarbocyanine J-aggregates at $S = 40\%$ on an (001) AgBr microcrystal. (b) Vertical data along line X–Y in (a). The AgBr surface level is assumed to be at $z = 0$.



(a)

(b)

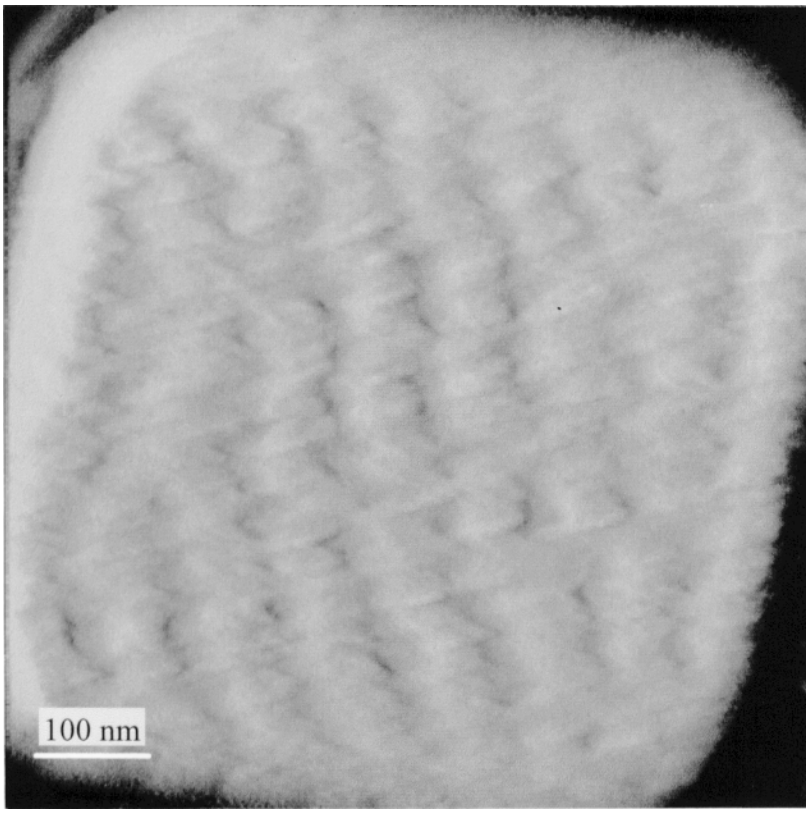
Figure 4. (a) AFM image of oxacarbocyanine J-aggregates at S = 10% on an (001) AgBr microcrystal. (b) Vertical data along line X–Y in (a).



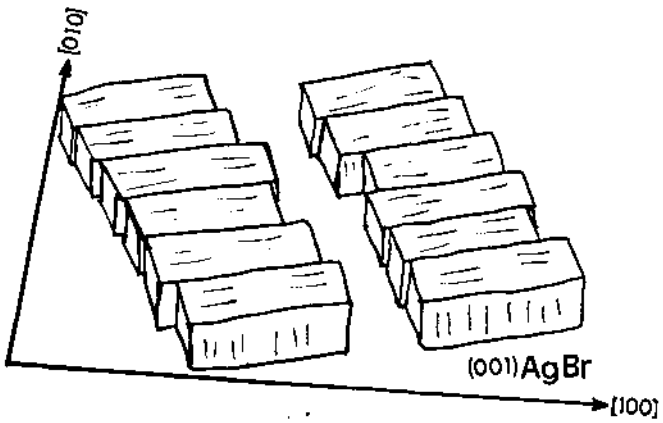
(a)

(b)

Figure 5. (a) AFM image of oxacarbocyanine J-aggregates at S = 40% on an (001) AgBr microcrystal. (b) Vertical data along line X–Y in (a). The AgBr surface level is assumed to be at z = 0 and line X–Y has a gradient of 2.8/1000.



(a)



(b)

Figure 6. (a) AFM image of oxacarbocyanine J-aggregates at S = 40% on an (001) AgBr microcrystal. (b) Schematic representation of stripes constructed with rectangular J-aggregate particles.

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