Island Formation and Layer Growth of Photosensitizing Dye J-Aggregates on AgBr Microcrystals Grown in Gelatin

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Growth mode of thiacarbocyanine J-aggregates with counter ions of different electronic charges is examined, referring to our previous studies with X-ray photoelectron spectroscopy (XPS), cathodoluminescence electron microscopy, high-resolution scanning electron microscopy, (SEM) and atomic force microscopy (AFM). A reinvestigation of the previous XPS studies suggests the dyes nucleate in solution and adsorb onto AgBr microcrystals in gelatin to form multilayered islands in Volmer-Weber growth mode,[1] rather than in Van der Merwe type monolayer adsorption. Microscopic studies clearly supported the island-growth mode of J-aggregates on AgBr emulsion crystal surfaces, and the height of each J-aggregate island was measured to be a multiple of unit thickness. However, the number of J-aggregate monolayers in one unit thickness differed with the type of counter ions of the dye.

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Introduction

Silver halide photographic materials extend their sensitivity to longer wavelengths with the help of cyanine dyes adsorbed on the surface. The dyes, so-called photosensitizing dyes, form nuclei of J-aggregates[2] (named after Dr. Jerry[3] who discovered them) on the surface or in the solution near the surface of silver halide microcrystals, and the nuclei are adsorbed on the surface to grow as aggregates. Growth mechanism and the adsorption process for the aggregates have been studied mainly with optical spectroscopic and/or electrochemical methods. Crystallographic or microscopic information including shape, size, adsorption site, molecular arrangement, and crystal structure of J-aggregates have long been veiled. Cyanine dye J-aggregates are believed to adsorb with their crystal axes or molecular plane a definite angle with respect to the substrate silver halide lattice. In spite of the high sensitivity of silver halides to probing with electrons or X-rays, rapid progress in structural analysis methods and surface science technology enabled us to form visual images of the adsorption of dye molecules and their aggregates on silver halide crystal surfaces. Electron spectroscopic methods are also useful to study adsorption interactions between cyanine dyes and substrate silver halides.

The method of transmission electron microscopy with selected area electron diffraction has successfully been used to study organic microcrystals epitaxially grown on solid surfaces. Thin films of the microcrystals are usually removed from the substrate crystals and placed onto a specimen holding mesh for transmission electron microscopes and studied by electron diffraction. However, this method does not work well for J-aggregate adsorption on silver halides. Once the specimen has been soaked in sodium thiosulfate aqueous solution, the substrate silver halide microcrystals dissolve away and the dye aggregates becomes free from the substrate. However, the detached aggregates undergo disruption of the structure from attack of surrounding water. On the other hand, the substrate AgX crystals are too thick for probing electrons to observe dye aggregates in the adsorbed state.

We first visualize the size of J-aggregates on practical AgBr emulsion microcrystals with our cathodoluminescence electron microscopy [analytical color fluorescence electron microscopy (ACFEM)].[4,5] The luminescence detection in a scanning electron microscope gives a map of light emitting materials on the specimen, and the size, number, and position of adsorbed dye J-aggregates are measured on AgBr microcrystals grown in gelatin. Electron irradiation causes a change of luminescence color[6] reflecting electronic states of the aggregates, which is the same process as that by which the dye aggregates absorb light in photographic film.

Low energy electrons carry back information of surface-related structures of the specimen. Electrons less than 1 keV or so have another advantage in studying photographic materials; the electrons expose silver halide far less than those of 2 keV or higher.[7] The clear images of narrow stripes of the J-aggregates are visualized accordingly.[8,9]

Very recent developments in scanning force microscopes brought visual images of solid surfaces. Atomic scale observations of (111) surfaces of AgBr were undertaken to reveal the surface reconstruction. However, few studies with atomic force microscopy were made on the structure of adsorbed J-aggregates grown in gelatin. Scanning tunneling microscopy (STM) is also effective and the highest-resolution technique to probe surface topography, but it can be limiting in application to electroconductive substrates. So, practical photographic materials are generally excluded from STM applications.

In this paper, we discuss layered structures grown in islands of thiacarbocyanine J-aggregates with counter ions of different electronic charge, referring to the previous studies with atomic force microscopy (AFM).[10] X-ray photoelectron spectroscopy (XPS),[11,12] Auger spectroscopy (AES),[13] ACFEM,[2,4,5] and high-resolution scanning electron microscopy (HRSEM).[7,8,9]

Experimental

Studies with XPS. Substrates used for XPS studies were silver chloride fused crystal plates for IR spectros-

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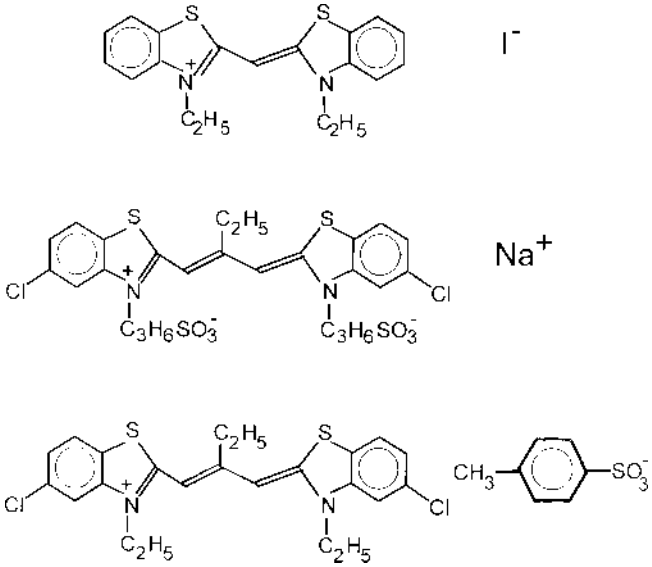


Figure 1. Dyes and their counter ions used. From top, Dye-I, Dye-Na and Dye-tosyl.

copy or AgBr octahedral microcrystals, 1 μm in size, grown in gelatin. Fragmentation by enzymlysis with centrifugal separation removed gelatin from the specimen. The XPS signal intensity analysis showed that amino acids on the AgBr microcrystals decreased to less than 1 % of the original. Silver deposited quartz plates (Ag quartz) were also used as a reference.

The adsorbate was 3,3'-dimethyl-1-9-ethylthiacarbocyanine dissolved in a mixture of water-methanol solution at concentrations of 10^{-4} to 10^{-7} mol/mol AgBr. Iodide was chosen as a counter ion (Dye-I) to distinguish from substrate chloride or bromide ions in XPS spectra. The dye molecule has a positive charge. All the substrate materials were soaked in the dye solutions for 30 min at 313 K, and dried after centrifugation. Adsorbed dye amount were calculated from residual dye concentrations after the adsorption. Potassium iodide of (10^{-6} to 10^{-3} mol/l aqueous solution) was also used as a reference adsorbent.

In XPS measurements, the following peaks were chosen to represent substrates, Ag_{3d}, Cl_{2p}, Br_{3d}, and for the dye and its counter ion, S_{2p}(dye) and I_{3d}. Spectra were signal-averaged and smoothed, and peak intensities (peak areas) were measured.

Low-Voltage High-Resolution Scanning Electron Microscope. Silver bromide cubic crystals, 0.7 μm in size, were grown in gelatin. Thiacarbocyanine dyes with two different types of counter ions; sodium ion (Dye-Na) and *p*-toluene sulfonic acid (Dye-tosyl), were used (Fig. 1). A dye molecule in the former case takes a negative charge, and in the latter a positive. These dyes in aqueous solutions of several different concentrations were added to the gelatin sols at the end of ripening, and the quantities of adsorbed dyes were calculated from the residual concentrations of dye solutions. The specimen were freed gelatin by enzymlysis, centrifuged, washed, and stored dry. We established that little gelatin remained on the AgBr surface by XPS[12] and by SEM.[13] The crystals were placed directly on the specimen holder with a liquid N_2 cooling system for the scanning electron microscope. Some of the specimens were prepared in the same manner for the AFM study (see AFM section) on flat electroconductive (ITO) plates.

The adsorbed quantity of dyes is given by a nominal monolayer percent coverage, i.e., the percent coverage of dyes on the substrate surface compared to the dye in the monolayer coverage. In the case of multilayered stacking, the area of surface covered by the dye decreased.

Low-voltage high-resolution SEM observation was performed with a Hitachi S-5000 microscope that resolves 0.6 nm at 30 keV incident beam and 3 nm at 1 keV or less. SEM draws surface topography from the difference in secondary electron yields. The escape depth of electrons in solids increases with their energy higher than 60 eV, and at 1 keV electrons can escape from about a 1-nm depth. We employed acceleration voltage, 700 V, and the beam current 0.6 or 2.2 pA. Each micrograph scan takes 80 s. However we did not use a liquid N_2 cooling specimen stage because of the electronic charge accumulation on the specimen surface at low temperature.[8] The specimen was kept at room temperature throughout the observation. Electron irradiation damage was checked by the method described in the previous reference.[7]

Studies with AFM. Two-dimensional arrangement of 0.7-μm AgBr microcrystals was prepared by the special method by Heki and Inoue,[14] repeating cycles of vigorous agitation in warm water and decantation. After several cycle times, most gelatin is removed and finally a two-dimensional close-packed film of AgBr particles appears floating on the solution. No enzyme treatment to fragment gelatin was employed. The floating film is placed on a flat electroconductive ITO plate for the observation.

The (001) AgBr surfaces with dyes were observed in contact static mode AFM at room temperature in an ambient air with a TopoMetrix TMX-2000 scanning probe microscope. The movement of the probe is detected with 670-nm laser light that scarcely exposes the specimen. The present system can draw surface topography maps on either trip of probe movement separately in one frame scan, and the comparison of these maps enabled us to identify artifacts in the image caused by the touching probe movement.

Results and Discussions

Studies with XPS. We reinvestigated the previous studies[11,12] to elucidate growth mode of J-aggregates. Figure 2(a) (middle left in Fig. 2) shows XPS signal intensity variation on dye-I adsorption on a AgCl fused crystal plate.[11] Dye signal, S_{2p}, was found on every substrate surface with dye adsorption treatment. A parallel decrease of both substrate signals with simultaneous increase of dye signals is interpreted to mean multilayered stacking of continuous dye molecules, as substrate signals receive repeated attenuation passing through the multistacked adsorbed dye layers. The counter ion signal, I_{3d}, could not be detected from the adsorption layer when the dye concentration of solution was 10^{-6} mol/l, which may indicate that dye molecules adsorb without accompanying iodine atoms or iodide counter ions. The I_{3d} signal appeared when the dye concentration was at 10^{-5} mol/l, and grew with dye concentration increase, suggesting the necessity of counter ions to form the second dye layer and so forth.

The specimens with dye-I adsorption on AgBr emulsion for XPS study[12] were prepared in two ways, with and without gelatin. The results from both specimens agreed fairly well. Optical absorption spectra of the specimen AgBr showed the J-aggregate peak of the dye at about 640 nm, red-shifted by refraction due to AgBr microcrystals. The dye signal, S_{2p}, appeared to a significant extent at a certain concentration as marked by the arrow in Fig. 2(b) for the specimen with gelatin (middle right in Fig. 2); the specimen without gelatin showed the same tendency. It increased

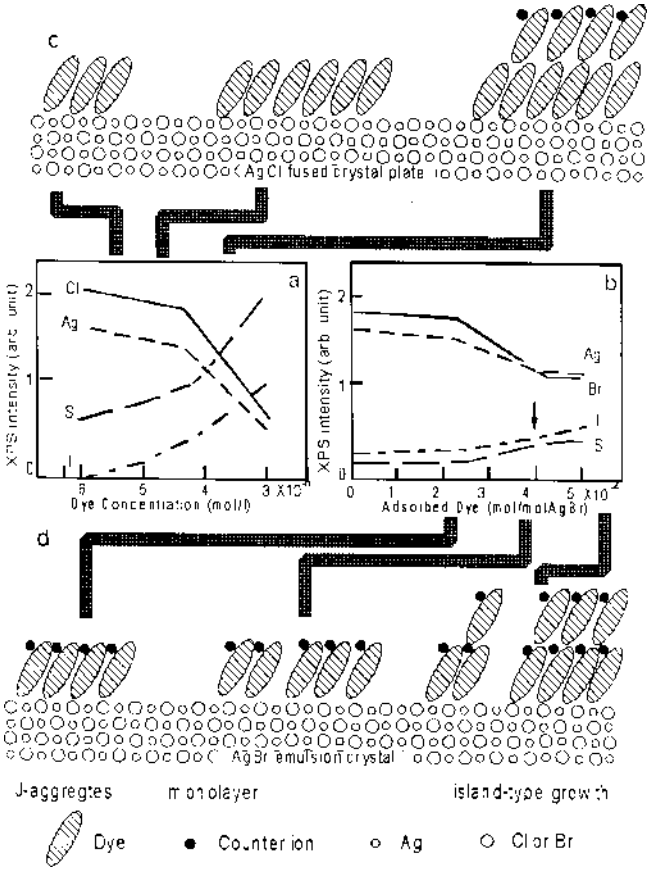


Figure 2. XPS signal intensity variations with Dye-I adsorption; (a) on AgCl fused crystal plate, (b) on AgBr microcrystals grown in gelatin. Schematic diagrams of Dye-I adsorption on (c) a AgCl plate and (d) on AgBr emulsion crystals . All figures are redrawn from Refs. 11 and 12.

gradually with dye concentration. This onset of dye signal intensity suggests that the dye adsorption is not in molecular form but in a cluster or in the form of a molecular assembly. In other words, the J-aggregates are not assembled on the surface from isolated dye molecules adsorbed on the surface. J-aggregates are formed (or nucleated) in the solution in advance of adsorption, with counter ions to keep the charge neutral, and, after adsorption on silver halide crystals, they grow in size from the reservior of dye molecules in solution. This nucleation and adsorption mechanism is also supported by the observation[2] with ACFEM on particles of cube, octahedron, and cubocta-hedron AgBr.

The slow decay of substrate signal with the intensity increase of the dye [Fig. 2(b)] must be of the next interest. If the dye layer forms a continuous film to cover the substrate surface as was discussed for dye adsorption on AgCl fused crystals [Fig. 2(a)], we should expect rapid decrease of the substrate signals with dye adsorption. The observed slow intensity decrease with adsorption in Fig. 2(b) is attributed to a contribution of signal electrons arriving directly at the detector without passing through the adsorbed layers, i.e. the dye aggregate layer contains many holes or gaps which the substrate signal electrons can pass through without suffering attenuation. This type of film appears when the adsorbed layer grows in the Volmer-Weber growth mode,[1] the so-called island growth mode.

Figure 2(c) and 2(d) are schematic models of the dye adsorption on AgCl plate and AgBr emulsion crystals. On the AgCl plates, dyes seem to adsorb without forming J-aggregates. However, on AgBr emulsion crystals, the dye adsorbed after forming J-aggregates and never completed the continuous overlayer film. Accordingly the nuclei of J-aggregates must be made before adsorption.

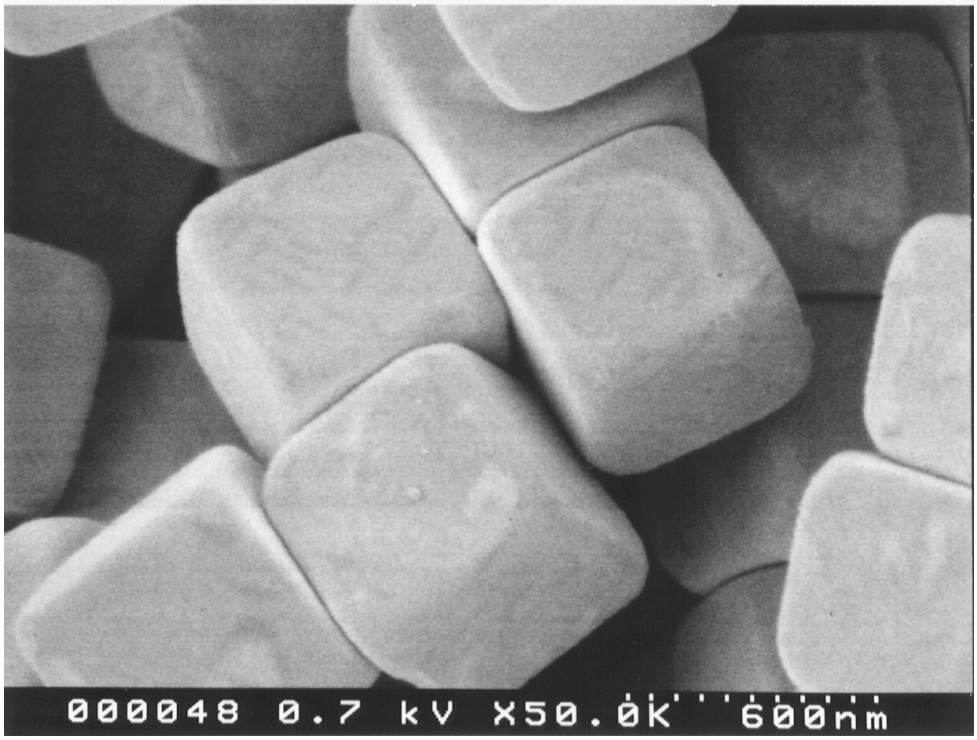
Low-Voltage High-Resolution SEM Study. Figure 3(a) shows island growth of Dye-Na. The specimen was provided at a different time from that of the previous study.[8] The dye coverage is 10% if all dyes form a monolayer. Parallel stripes as were clearly seen as in the previous study, again running along [210] directions on the surface. The stripes differ in length and do not cross each other. The density of parallel stripes is clearly sparser than that of the previous observation[8] and also of Fig. 3(b) at 40% dye.

Figure 3(b) is obtained when the dye quantity is increased to coverage corresponding to 40% of the monolayer. Some of the dye stripes grow wider, while others stay narrow as in Fig. 3(a). The wide ones are generally irregular in shape and they must be bundles of narrow stripes coalesced parallel within the image resolution. One of the edges, generally the longer side, of the individual dye aggregate deposits remain aligned along the [210] direction of the substrate AgBr (001). There are many wide area of bright flat contrast between the dye islands illustrated dark in the image, and the area accumulation of dye islands does not seem to reach 40% of the substrate surface that would be the area covered if the dye adsorbed in monolayer.

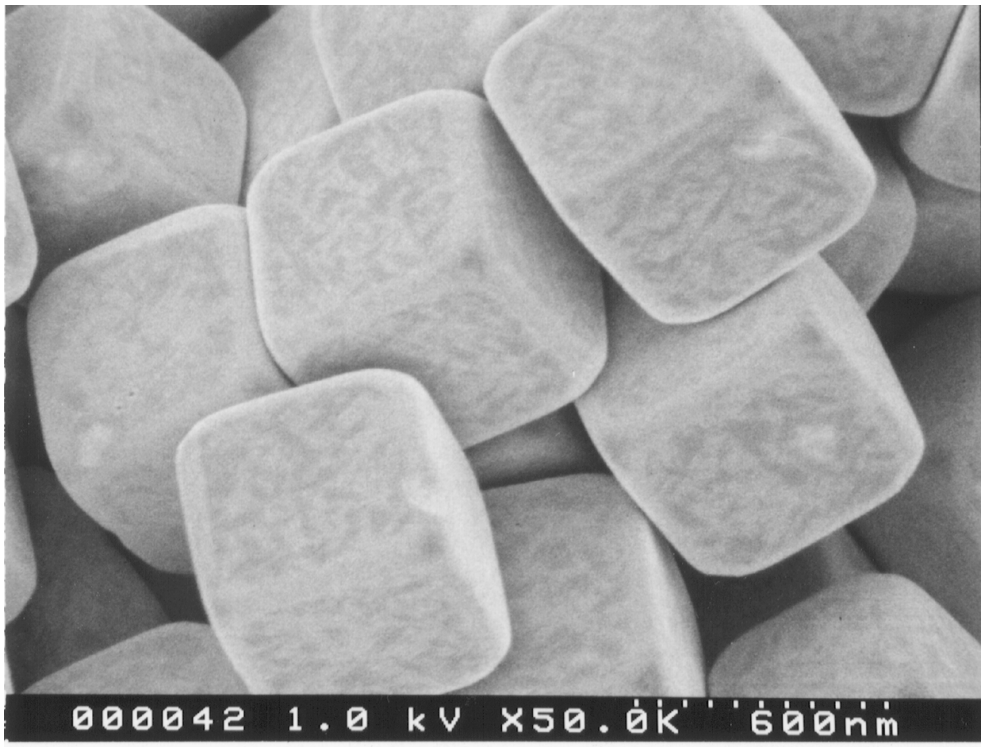
AFM Study. An AFM image of Dye-Na J-aggregates on a AgBr surface with nominal monolayer coverage of 10% is shown in Fig. 4. We ascribe stripes or islands to J-aggregates, which align like ripples bending parallel to various directions at almost the same spacing. As an AFM image is a convolution of the probe shape and the specimen structure, the bottoms of the ridges are always depicted wider and the grooves shallower than the real specimen. The top face of projected structures are usually imaged correctly in size, so we can measure the width of the stripes from Fig. 4. The widths do not differ much on any stripes, which suggests the stripes to be assembled of modular J-aggregates. We suppose the module to be similar to that observed by highly resolved AFM imaging for oxacarbocyanine in Fig. 6 of Ref. 10. A vertical analysis of an enlarged observation[10] of the same specimen suggests that the stripes or islands grow with thickness of multiples of 2.1 nm and with widths of several tens of nanometers.

Figure 5(a) is an AFM image of Dye-tosyl at 10% nominal coverage. Figures 5(b), 5(c), and 5(d) are vertical data along $X_1 - X_2$, $Y_1 - Y_2$ and $Z_1 - Z_2$ correspondingly in Fig. 5(a). To accomplish the height analysis of the figures, we first determine the basal plane for Figs. 5(b) to 5(d). There lacks a flat area in these figures. As the line $Z_1 - Z_2$ runs on the ridge of dye islands, we drew a line along the top of the height curve in Fig. 5(d). Then parallel lines of the same distance could be drawn to pass every significant terrace or kink on the curve in Fig. 5(d), and we got the line distance 1.04 nm that is just a half obtained for Dye-Na. Next we analyzed Figs. 5(b) and 5(c) with the 1.04-nm thickness for a dye layer. As the lines $X_1 - X_2$ and $Y_1 - Y_2$ are parallel to each other in Fig. 5(a), the base lines for Figs. 5(b) and 5(c) must have the same inclination. The parallel lines shown in the figures satisfy all the requirements and pass through important points on the vertical data. Thus the aggregates of Dye-tosyl grew in stripes with n (n = 1 – 10) unit layers 1.04 nm thick.

The structure of J-aggregates of Dye-tosyl grown in solution has been analyzed[15] by a conventional X-ray crys-



(a)



(b)

Figure 3. (a) Dye-Na J-aggregates adsorbed on AgBr microcrystals grown in gelatin. Nominal adsorption quantity is 10% in the monolayer. (b) Dye-Na J-aggregates adsorbed on AgBr microcrystals grown in gelatin. Nominal adsorption quantity is 40% in the monolayer.

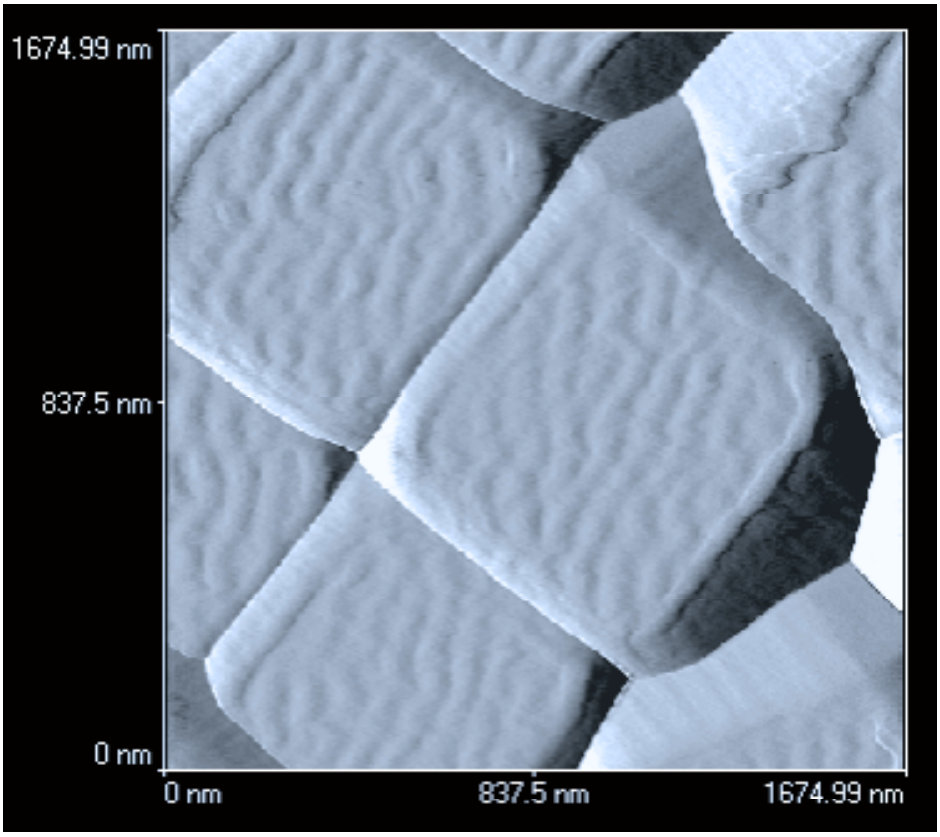
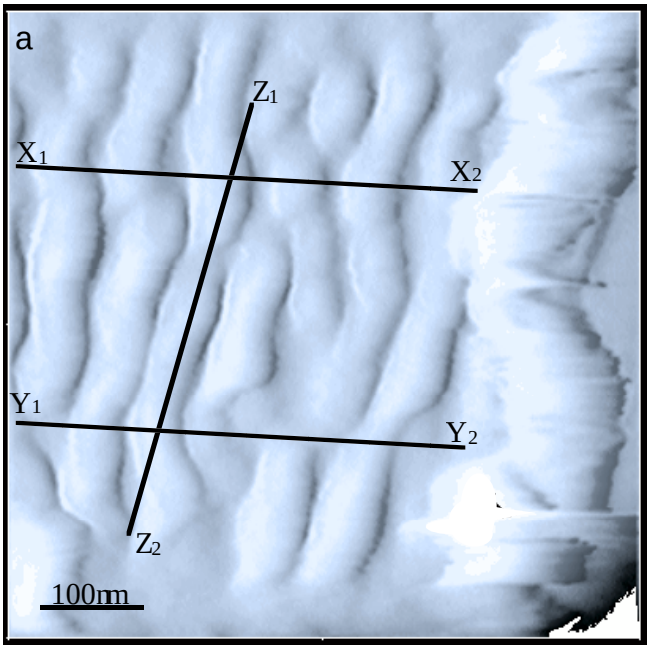


Figure 4. AFM images of Dye-Na J-aggregates at nominal adsorption quantity 10% on (001) AgBr microcrystals.



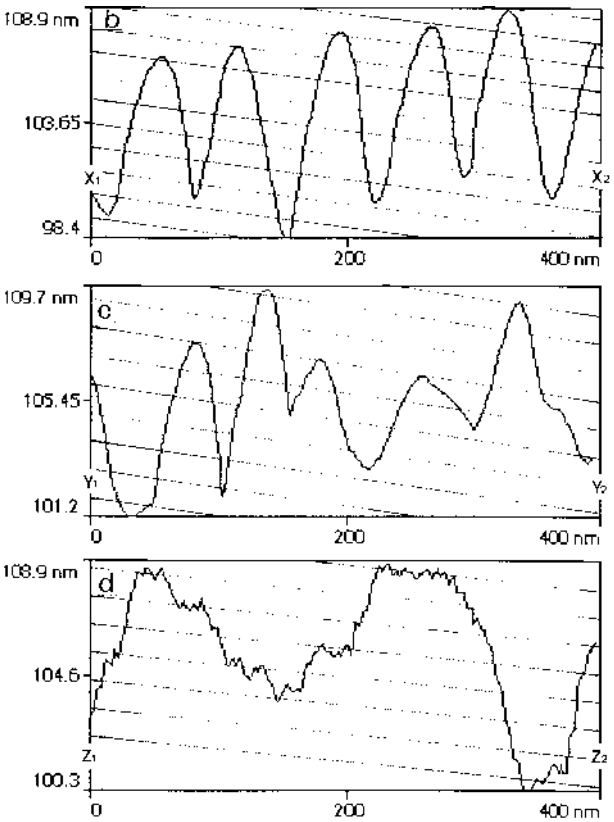


Figure 5. (a) AFM images of Dye-tosyl J-aggregates at nominal adsorption quantity 10% on (001) AgBr microcrystals. (b), (c), and (d): Vertical data along $X_1 - X_2$ or $Y_1 - Y_2$ lines in (a). Line spacings in the figure, 1.04 nm.

tallographic method, and the *b* axis, repeating unit of dye layers, is given as $b = 2.1$ nm. In the 2.1-nm unit, two dye monolayers and two counter ion layers are included intercalating each other, i.e., one dye monolayer is always accompanied with one counter ion layer. The AFM vertical data in Fig. 5(a) for Dye-tosyl adsorption reveal that the dye grew with a unit of one dye monolayer and corresponding one counterion layer, and the spacing is about half of the *b*-axis dimension. The other dye, Dye-Na grew with 2.1 nm per unit.[10] This value is equal to the unit cell length of the *b* axis for Dye-tosyl, i.e., the double dye monolayers and corresponding counter ion layers. Throughout the AFM observation for Dye-Na, we could not find a 1-nm-thick layer in the vertical data, and therefore we are convinced that the 2.1-nm-thick layer cannot be divided into two equivalent layers. The geometry of dye and counterion layers in this 2.1-nm-thick unit is not known from the present study.

The difference in the electronic charge of dye molecules (or counterions) might affect the conformation of the unit layer. X-ray analysis of a Dye-Na J-aggregate crystal structure will provide information of the unit layer structure. Whatever the unit layer may be, J-aggregates grow with a stack height of 10 or more unit layers. We should hence emphasize that the J-aggregate islands formed by the Volmer-Weber growth mode, rather than in monolayer adsorption.

Conclusion

Cyanine dyes adsorb on AgBr emulsion crystals after the nucleation of J-aggregates near or on the surface. The aggregates grow with a supply of dye molecules from the surroundings, forming islands or stripes by the Volmer-Weber growth mode[1] rather than in monolayer absorption. AFM observations showed that the dye islands grew in layers, and the thickness of unit layer varied with dye species. Dye-Na grew with double dye monolayers, while Dye-tosyl and oxacarbocyanine[10] grew by individual monolayers. In either case the same number of counterions as dye molecules must be included in each unit layer. Observed thickness of stripes varied one layer increments to 10 or more. The J-aggregate layer is thus composed of J-aggregate modules several tens of nanometers in size.[6,13] In a highly resolved AFM image of oxacarbocyanine, stripes were constructed from a multiplicity of rectangles [20 × (35 – 50) nm in size],[10] and the rectangles were regarded as element crystallites or modular J-aggregate particles photoelectronically separated with each other.

Most of the present samples were prepared by repeated warm-water dilution with vigorous agitation and decantation to get rid of gelatin,[14] excluding the condensation process that is encountered using enzyme and centrifugal separation to remove gelatin. We thereby believe that the AgBr surfaces observed in this study corresponds to the true nature of practical emulsion crystal surfaces. We further mention that the island growth of photosensitive dye is not a special case in merocyanine dye film, observed by Haefke et al.,[16] but generally takes place in practical dyes. ▲

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References

1. e. g., I. Markov, *Mater. Chem. Phys.* **9**, 93 (1983).
2. H. Saijo, T. Isshiki, M. Shiojiri, S. Watanabe, T. Tani, and K. Ogawa, *J. Imag. Sci. Technol.* **39**, 539 (1995).
3. E. E. Jerry, *Nature* **138**, 1009 (1939).
4. H. Saijo, T. Isshiki, M. Shiojiri, H. Ohtani, G. Ning, and K. Ogawa, *Proceedings of the Intern'l East-West Symposium III, New Frontiers in Silver Halide Imaging* (Hawaii, 1992), B37-41.
5. H. Saijo, T. Isshiki, M. Shiojiri, H. Ohtani, G. Ning, and K. Ogawa, *J. Imag. Sci. Technol.* **37**, 348 (1993).
6. H. Saijo, T. Isshiki, M. Shiojiri, G. Ning, and K. Ogawa, *J. Imag. Sci. Technol.* **38**, 217 (1994).
7. H. Saijo and M. Shiojiri, *Phys. Stat. Sol. (a),* **148**, K85 (1995).
8. H. Saijo, T. Isshiki, and M. Shiojiri, *J. Imag. Sci. Technol.* **38**, 455 (1994).
9. H. Saijo and M. Shiojiri, *J. Cryst. Growth* **153**, 31 (1994).
10. H. Saijo and M. Shiojiri, *J. Imag. Sci. Technol.* **40**, 111 (1996).
11. H. Saijo, T. Kitamura, and H. Ohtani, *Surf. Sci.* **177**, 431 (1986).
12. H. Ohtani, T. Kitamura, and H. Saijo. *J. Imag. Sci.* **32**, 43 (1988).
13. H. Saijo, T. Isshiki, M. Shiojiri, and H. Ohtani, *J. Imag. Sci. Technol.* **37**, 314 (1993).
14. T. Heki and N. Inoue, *Forma* **4**, 55 (1989).
15. H. Asanuma, K. Ogawa, T. Tani, and J. Tanaka, Preprint of Symposium on Molecular Structure, 1994, Tokyo, 2D15 (Japanese).
16. H. Haefke, U. D. Schwarz, H. -J. Güntherodt, F. Fröb, G Gerth and R. Steiger, *J. Imag. Sci. Technol.* **37,** 545 (1993).