Terrace Formation of Cyanine Dye J-aggregates on AgBr Microcrystals Grown in Gelatin

Hiroshi Saijo,*,‡ Katsutoshi Tanabe§ and Makoto Shiojiri†,¶

Department of Electronics and Information Science, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585 Japan

Photosensitizing dyes are required to stretch the sensitivity of silver halides for photographic use to the full wavelength of visible light. The growth of silver halide microcrystals and adsorption of dyes in the form of J-aggregates onto them are performed in gelatin sol. The dye adsorption has been thought to occur homogeneously on every particle of silver halides. However cathodoluminescence microscopy revealed that the quantities of adsorbed dyes on the particles differ significantly. The island growth of dye aggregate layers becomes clear by low-energy high-resolution scanning electron microscopy and atomic force microscopy. The islands align parallel and form a terrace on most particle surfaces of AgBr. In the area out of the terrace region, there are little dyes in adsorption. The concentration of adsorbed dyes in the terraces on certain particles of AgBr result in a deficiency of the aggregates in adsorption on other particles.

Journal of Imaging Science and Technology 43: 89–93 (1999)

Introduction

Silver halides have been long a sole king of photographic recording materials having both sensitivity and quality. However, the lack of sensitivity of silver halides to green and red light requires adsorption of dyes that release photoelectrons on absorption of long-wavelength lights. Photographic films must respond to exposing light with equal sensitivity, and, therefore, the dye adsorption is expected to be homogeneous throughout the photographic material.

However, this homogeneous adsorption of J-aggregates has hardly been examined by crystallographic analyses, and remains as a hypothesis. In studies[1–3] with cathodoluminescence (CL) microscopy (ACFEM[4]), we observed intensity variations of the luminescence of J-aggregates on the surface of AgBr. Because the luminescence intensities are proportional to the populations of aggregates, it is possible to count how many aggregates in regard to their orientations are on AgBr particles. However, the strong difference in luminescence intensities of each particle surface convinced us that the adsorption of cyanine dye J-aggregates is not homogenous.

In the previous paper[1] we described significant differences of dye quantities adsorbed on AgBr microcrystals. The nucleation of the J-aggregates occurs near or on the surface of AgBr, and the nucleus adsorbs on the surface of AgBr near the place of nucleation and continues to grow with a supply of dye molecules from the surrounding solution.[2] The J-aggregates stack in multilayer islands, which is confirmed by atomic force micro-scopy (AFM).[5]

Low-energy high-resolution scanning electron microscopy (LESEM) brought us crisp images of dye J-aggregates on AgBr microcrystals.[6] The aggregates aligned linearly contacting each other with their edges to form linear stripes along [210] directions on the (001) surface of AgBr, and the stripes gathered in parallel taking a shape of a patch or terrace. The lower side to the edge of the terrace looks flat, and no adsorbing material is noticed with 700 eV primary electrons. The AFM observations revealed that the J-aggregate stripes are mountainous with heights more than 10 dye monolayers.[5] The concentration of adsorbed J-aggregates in the mountainous arrays might affect the population distribution of dye aggregates to other particles.

In this report, we discuss, with CL microscopy, LESEM, and AFM observations, the terrace formation of J-aggregates adsorbed on AgBr crystal surfaces grown in gelatin.

Experimental

The specimen preparation method was the same as in the previous study.[1] Thiacarbocyanine dyes with two different types of counter ions, sodium ion (thiacarbocyanine-Na) and *p*-toluene sulfonic acid (thiacarbocyanine-tosyl), and an oxacarbocyanine were used in the study (Fig. 1). The dye molecules were adsorbed on silver bromide cubic crystals, 1 or 0.7 mm in size in gelatin sol. Two different methods were employed to remove gelatin of the specimen for microscopic observations. One method is a conventional method with fragmentation of gelatin by enzyme, followed by centrifugal separation, washing, and stored dry. The specimen powder is placed on the specimen holder for the scanning electron microscope. The other is to provide two-dimensional

Original manuscript received December 8, 1997

* IS&T Life Member

† IS&T Member

‡ Fax: +81-(0)75-724-7446, e-mail: hsaijo@dj.kit.ac.jp

§ Ehime Univ., Fax: +81-(0)89-927-9396: ktanabe@edserv.ed.ehime-u.ac.jp

¶ Fax: +81-(0)75-723-2048, e-mail: shiojiri@dj.kit.ac.jp

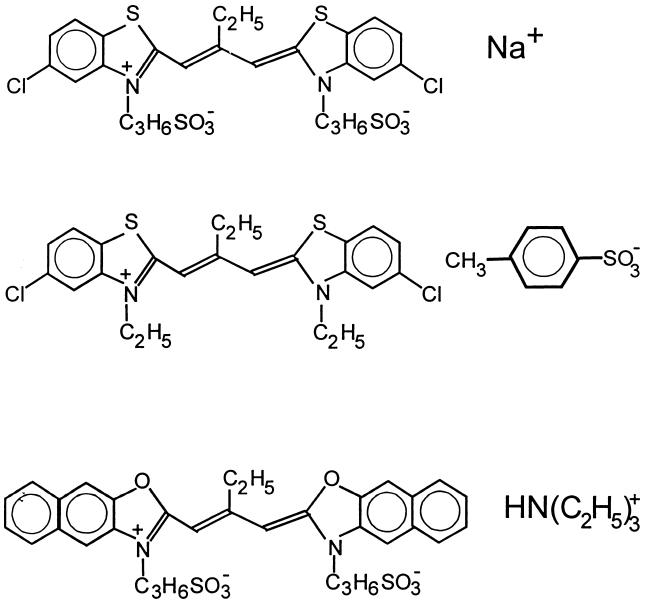

Figure 1. Cyanine dyes used in the study. (a) 3,3'-bis-sulfopropyl-5,5'-dichloro-9-ethyl-thiacarbocyanine sodium salt (thiacarbocyanine-Na); (b) 3,3'-bis-ethyl-5,5'-dichloro-9-ethyl-thiacarbocyanine *p*-toluene sulfonic acid salt (thiacarbocyanine-tosyl); (c) 3,3'-bis-sulfopropyl-5,6,5',6'-dibenz-9-ethyl-oxacarbocyanine triethyl ammonium salt (oxacarbocyanine).

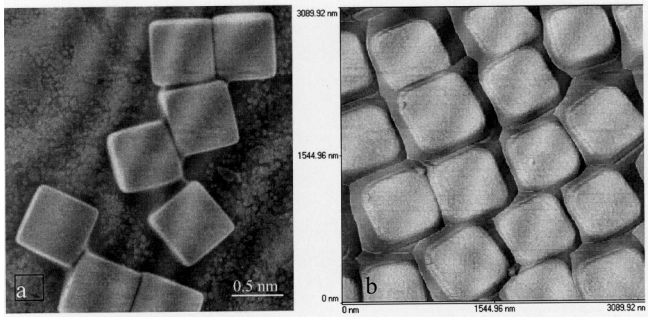

Figure 2. The surface of AgBr cubic particles without dye adsorption. (a) LESEM observation, and (b) AFM observation.

arrangement of AgBr microcrystals with the special method by Heki and Inoue.[7] This method contains the following steps: A specimen with gelatin is washed repeatedly in warm water with strong agitation and finally a thin film of AgBr particles grows floating on the surface of the water. The thin film of AgBr is scooped onto flat electric conductive ITO (indium-tin oxide) plates and placed on specimen holders for microscopy.

The microscopes used were a Hitachi S-5000 scanning electron microscope at the Techno Research Center, Hitachi Instruments Engineering Co. Ltd. for LESEM, cathodoluminescence microscope (analytical color fluorescence electron microscope) for CL observation, and a TopoMetrix TMX-2000 scanning probe microscope, at the Scientific Instruments Center, Nissei Sangyo Co. for AFM. Details of the microscopic observations are described in previous articles.[1–6]

Results and Discussion

Population distributions of adsorbed dye J-aggregates on AgBr microcrystal surfaces were examined with CL patterns, SEM, and AFM. Micrographs of AgBr microcrystals without dye adsorption are shown in Fig. 2 taken

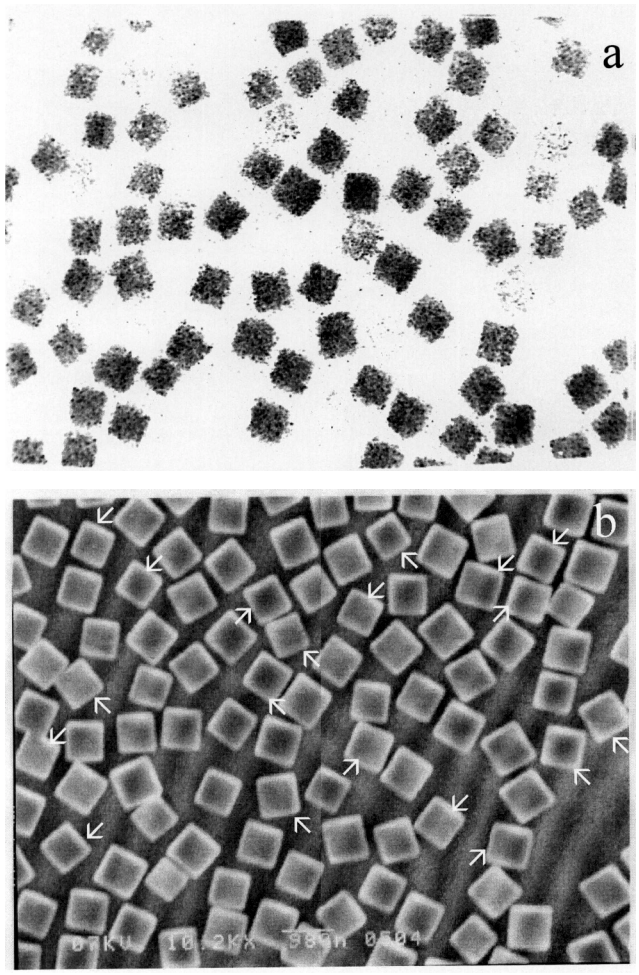

Figure 3. (a) Cathodoluminescence micrograph and (b) corresponding secondary electron image of thiacarbocyanine-tosyl dye J-aggregates. Some particles that show irregular distribution of adsorbed J-aggregates are noted by arrows.

with LESEM and AFM. Because the secondary electron image of the specimen with CL microscopy is almost the same as with LESEM and the CL image does not contain any contrast, CL observation is not included here.

Cathodoluminescence Microscopy. Cathodoluminescence micrographs describe distributions of dye J-aggregates on AgBr crystal surfaces with the pattern of bright spots of luminescence. Figure 3 is an example to show the difference of adsorption on each surface of AgBr particle. In the figure we show by the small arrows that some particles do not have homogeneous distributions of CL emitting J-aggregates. In the enlarged image of the same specimen, it becomes clear that the population densities of adsorbed J-aggregates are not the same on the surfaces. The luminescence from particle "a" in Fig. 4 comes mainly from the three quarters of the surface, and little from the remaining area. However the density of luminescence emitting points in the less populated area on particle "a" is almost the same as that from particle "b." Particle "c" has a more complicated boundary between a high- and low-populated area of luminescence emitting materials that is schematically illustrated in Fig. 4(a). Another example to show the difference of populations of adsorbed dye aggregates on AgBr is given in Fig. 5. Here again are particles of

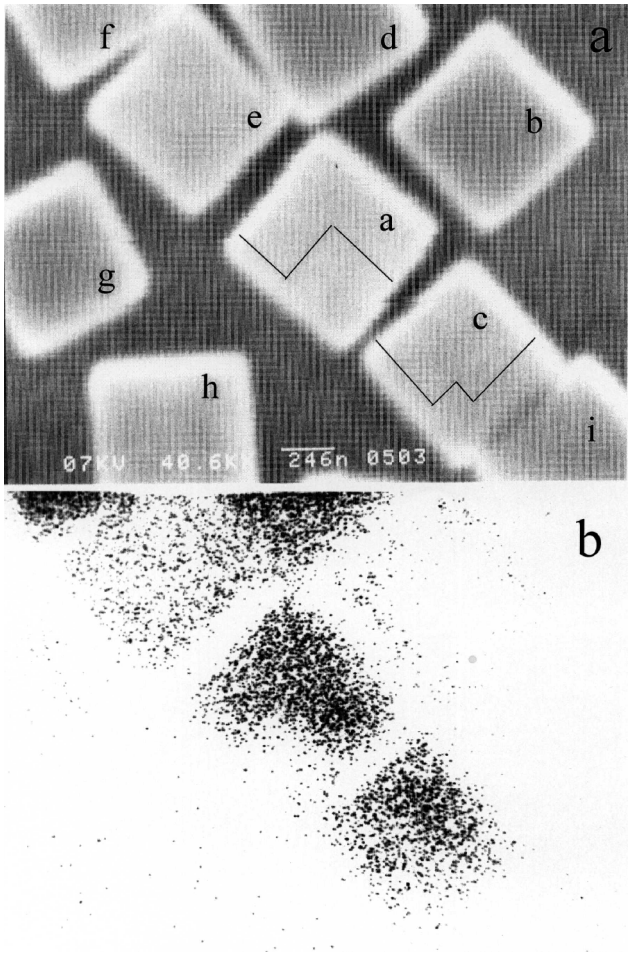

Figure 4. (a) Enlarged secondary electron image and (b) corresponding cathodoluminescence micrograph of the same specimen for Fig. 3. Three quarters of the surface of center particle "a" are covered with the dye J-aggregates, while the other area lacks adsorbed dyes. The borders between the high and low population of J-aggregates on particles "a" and "c" are illustrated in (a).

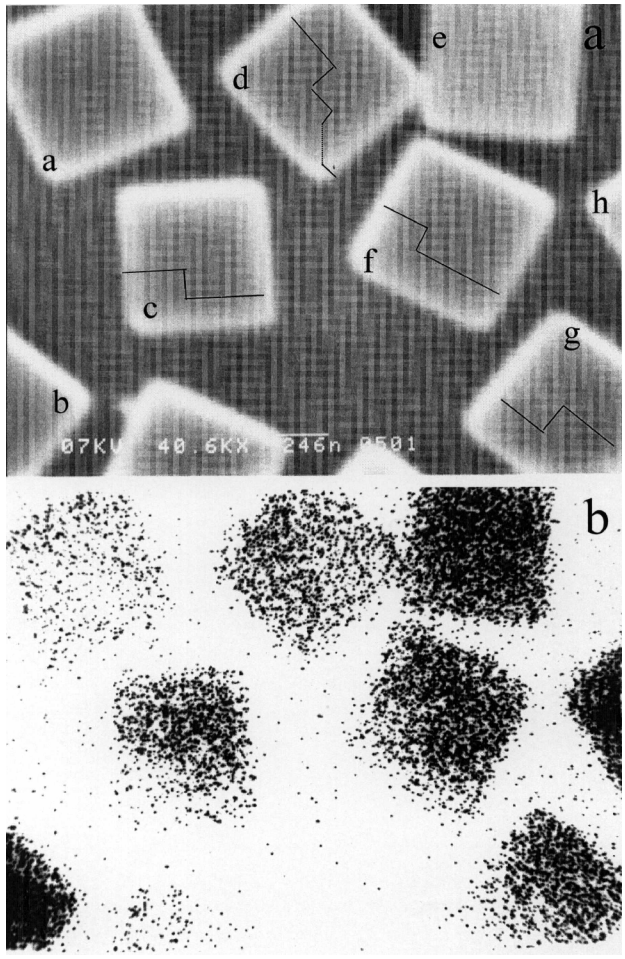

Figure 5. (a) Enlarged secondary electron image and (b) corresponding cathodoluminescence micrograph of thiacarbocyanine-tosyl adsorbed AgBr particles. The borders between high and low population of J-aggregates are illustrated in (a).

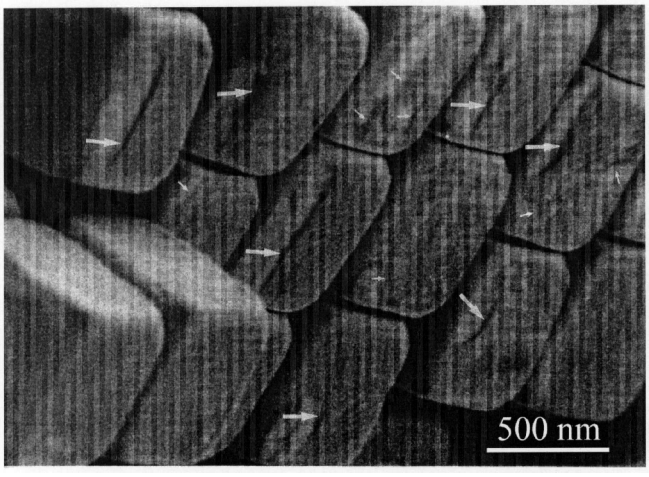

Figure 6. Thiacarbocyanine-Na J-aggregates observed on AgBr with ultra-low energy high-resolution SEM and reproduced from Ref. 6. White arrows point out the steps of the J-aggregate population.

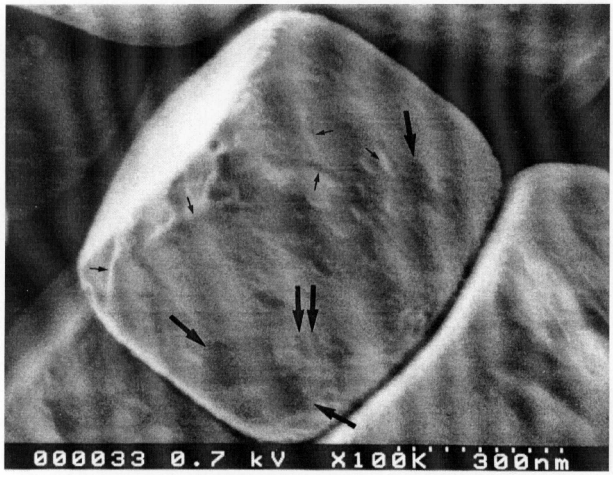

Figure 7. Oxacarbocyanine J-aggregates observed on AgBr with ultra-low energy high-resolution SEM. Small arrows indicate the steps of the J-aggregate population. Large arrows show the different orientation patches of J-aggregates.

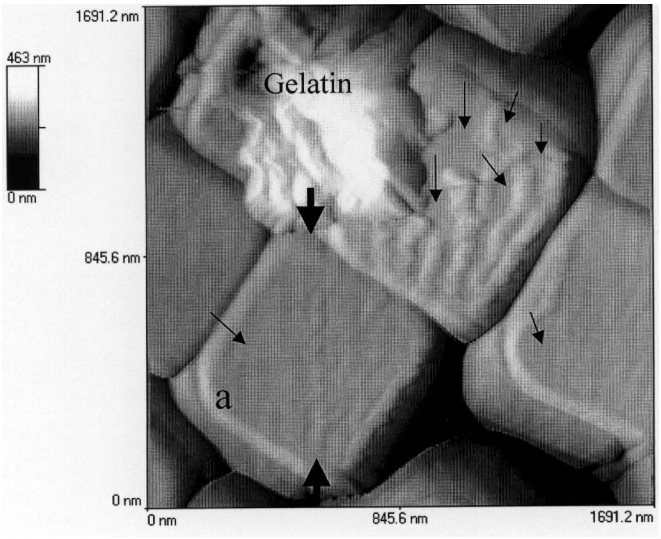

Figure 8. AFM image of oxacarbocyanine J-aggregates observed on AgBr. The dye quantity is 10% to occupy on the surface if monolayer adsorption. Small arrows indicate the flat zones. Bold short arrows indicate the border of the J-aggregate population.

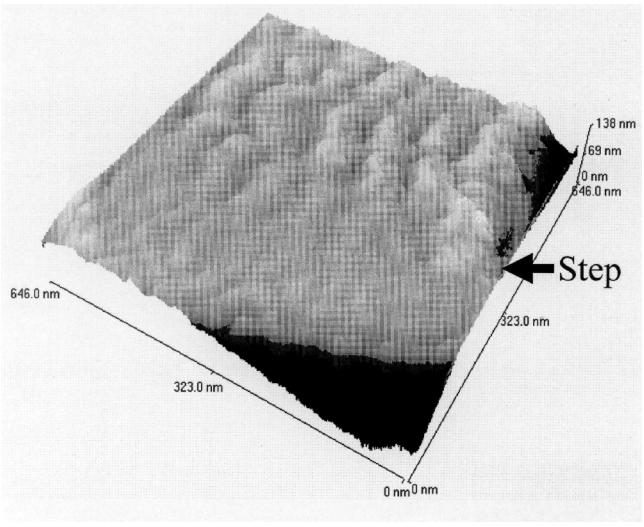

Figure 9. AFM image of oxacarbocyanine J-aggregates observed on AgBr. The dye quantity is 40% to occupy on the surface if monolayer adsorption.

densely adsorbed ("b", "e", and "h"), sparsely adsorbed ("a") and some in between the two. On particles "c", "d", "f", and "g", the boundaries between high- and low-luminescence populations are seen [as illustrated schematically in Fig. 5(a)]. Thus the population distribution of J-aggregates on every surface of AgBr particle is not homogeneous for various cyanine dyes on AgBr emulsion crystals.

Low-Energy High-Resolution Scanning Electron Microscopy. Scanning electron micrographs[6] of thiacarbocyanine-Na J-aggregates on AgBr provided images of linear columns of J-aggregate crystallites connected to each other by the edges. The columns of J-aggregates gathered aligning parallel to form terraces on many particles of AgBr as shown in many figures of Ref. 6, and one such figure is reproduced in Fig. 6. The white arrows in Fig. 6 indicate edges of the terrace, and on the terrace we can observe parallel lines of linearly aligned J-aggregate columns.

Oxacarbocyanine dye molecules build up low-profiled flat terraces that occupy most of the surface of AgBr (Fig. 7). The edge of each terrace is marked by a small black arrow. Dark rectangular patches in the terrace region marked by large arrows in Fig. 7 are the area where the dye molecules take a different orientation to the substrate lattice from that of the surrounding aggregates. In the lower side to the terrace edge, no special image contrast is seen with as low as a 700 eV probe beam. The inelastic mean-free-path data of electrons in many organic compounds[8] (IMFP, the length for electrons to traverse in solids without receiving inelastic scattering) indicate that the mean-free-path length has a minimum, 0.5 to 0.6 nm at about 60 eV, and increases linearly to 2 to 3 nm at 700 eV. The least IMFP, 0.5 nm, is almost equal to the thickness of the dye monolayer. The IMFP for higher energy electrons is large enough to pass a stack of few dye monolayers without suffering energy loss, and little image contrast is expected from the film of few dye monolayers. The dye adsorption in the lower side region to the terrace edge cannot be denied from the contrast of LESEM images.

Atomic Force Microscopy. Figure 8 is an AFM micrograph of oxacarbocyanine dye adsorption. Ten percent of the surface is covered by the dyes if they adsorb in monolayer. A tall mass is a residual gelatin (as marked). At the foot of the gelatin, there are flat contrast areas (some are noted by small arrows) surrounded by the rows. On the surface of particle "a", a vertical diagonal boundary (marked by bold short arrows) separates the surface to two zones: a structured contrast zone with rows (right half) and a low contrast zone (left half). The rows are J-aggregates as observed in ULESEM images. A vertical analysis across the boundary[9] shows that, in the low-contrast region, there are rows of J-aggregates 3 to 6 nm high, and in the high contrast zone the rows are 13 to 18 nm high. Another example of oxacarbocyanine adsorption is shown[10] in Fig. 9. Though the upper two thirds of the area is occupied by high mountainous rows, the lower side area contains low profiled rows a few nanometers high. The boarders between high and low rows in Fig. 9 and one on particle "a" in Fig. 8 must correspond to the steps seen in the ULESEM images, Fig. 6 and Fig. 7.

Conclusion

The population of adsorbed J-aggregates on the surface of the AgBr particle grown in gelatin differs significantly: Few AgBr particles with extremely concentrated or extremely little dye adsorption are found among the many particles on which surface the aggregates adsorb moderately. In spite of the significant difference of adsorbed dye quantities, no singularity was found on the shapes of substrate crystals in the secondary electron micrographs of CL observations.

Terrace formation is always observed on every surface of AgBr particles when J-aggregates adsorbed. J-aggregate crystallite particles connect to each other with

their edges like brick works to build up rows of a multi-layered mountainous stack. The multi-layered stacks of J-aggregates align parallel to make a continuous terrace.

The total quantities of dyes added to the specimen in the present study is nominally to cover 10 to 40% of the substrate surfaces of AgBr in monolayer. The multi-layered terrace formation requires more dyes than the monolayer adsorption of the nominal percenta coverage does, which causes little or no dye adsorption on some other particles.

The significant difference of J-aggregate quantities adsorbed on AgBr particles will cause heterogeneous response of the particles to the exposing light and the performance of photographic materials might be affected unfavorably. However the evaluation of it is beyond what we discuss here.

Acknowledgments. Specimen crystals were kindly prepared upon our request by Ms. S. Watanabe and Dr. T. Tani of Fuji Photo Film Co. Ltd. CL microscopy observation was made with the permission by Professor Emeritus the late K. Ogawa of Kyoto University. LESEM observation with Hitachi S-5000 scanning electron microscope was made by Ms. M. Nakagawa and Mr. M. Yamada, and AFM observation with TopoMetrix TMX-2000 was made by Dr. M. Hasemi. We appreciate their sincere cooperation.

References

1. H. Saijo, K. Tanabe and M. Shiojiri, *J. Imag. Sci. Technol.* **42** (1998).
2. H. Saijo, T. Isshiki, M. Shiojiri, S. Watanabe, T. Tani, and K. Ogawa, *J. Imag. Sci. Technol.* **39,** 539 (1995).
3. (a) H. Saijo, T. Isshiki, M. Shiojiri, H. Ohtani, G. Ning, and K. Ogawa, *J. Imag. Sci. Technol.* **37,** 348 (1993); (b) H. Saijo, T. Isshiki, M. Shiojiri, G. Ning, and K. Ogawa, *J. Imag. Sci. Technol.* **38,** 217 (1994).
4. T. Nakano, T. Fujimoto, H. Koike, and K. Ogawa, *Acta Histochem. Cytochem.* **23,** 753 (1990).
5. (a) H. Saijo and M. Shiojiri, *J. Imag. Sci. Technol.* **40,** 111 (1996); (b) H. Saijo and M. Shiojiri, *J. Imag. Sci. Technol.* **41,** 266 (1997).
6. H. Saijo, T. Isshiki and M. Shiojiri, *J. Imag. Sci. Technol.* **38,** 455 (1994).
7. T. Heki and N. Inoue, *Forma* **4,** 55 (1989).
8. S. Tanuma, C. J. Powell and D. R. Penn, *Surf. Interf. Analys.* **21**, 165 (1993).
9. Figure 4 in Ref. 5(a).
10. Figure 5 in Ref. 5(a).