Quantitative Evaluation of Spatial Uniformity in Spectral Characteristics for Large-area Colloidal Crystals

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We report a quantitative method for evaluating the optical quality of large-area colloidal crystals based on imaging spectroscopy. We measured the transmission spectra with the spatial resolution of large colloidal crystals having different optical quality and examined the characteristic features in terms of the standard deviation calculated on the basis of pixel-by-pixel transmittance of all pixels. As a result, it was possible to quantitatively characterize the difference between weakly and highly oriented samples prepared by a shear-induced method as a difference in the standard deviation in a pass-band wavelength region.

Colloidal crystals[1] are three-dimensional periodic arrays of monodispersed colloidal particles in a liquid medium. The lattice spacing of colloidal crystals is usually in the order of submicrometers, resulting in the photonic band gap effect[2] in the visible or near-infrared light region. Therefore, they have potential applications in optical filters, switches, and sensors.[3] Although polycrystalline samples can be easily prepared, the production of large single crystalline textures is a challenge for advanced studies pertaining to optical properties or applications. We have already found that a centimeter-order single domain could be tailored by running the colloidal suspension in a flat capillary cell,[4] according to the shear effect.[5] The angle-dependent transmission spectra and the laser-diffraction analysis—the Kossel line analysis[6]—in transmission geometry indicate that the sheared sample has a crystalline structure with a fixed orientation, as reported previously;[4] the (111) plane is parallel to the capillary face, and one of the closest packed directions in the (111) plane is parallel to the capillary axis in the face-centered-cubic (fcc) lattice. The crystal in the capillary also shows angle-dependent uniform diffraction colors, suggesting high spatial uniformity across a wide area. However, a versatile method for a more advanced evaluation of the uniformity from a spectroscopic point of view, which is necessary for practical applications as optical devices, has not yet been established.

In this paper, we report a spectroscopic method for evaluating the spatial uniformity for large-area colloidal crystals by adopting a statistical approach based on imaging spectroscopy in transmission geometry. We show that the uniformity over a large area for samples prepared by the shear-induced method can be quantitatively investigated by estimating the standard deviation of transmittance obtained from the spatially resolved spectrometry.

The large-area colloidal crystals were prepared as follows: A suspension of uniform-sized polystyrene microspheres (Duke Scientific Corp., Palo Alto, CA; particle diameter 198 nm; standard deviation 3%) in water with a particle volume fraction of ca. 10% was deionized using a mixed-bed ion-exchange resin (Bio-Rad, AG501-X8, Hercules, CA) in vials until the suspension showed iridescence indicative of a crystal phase. The crystalline

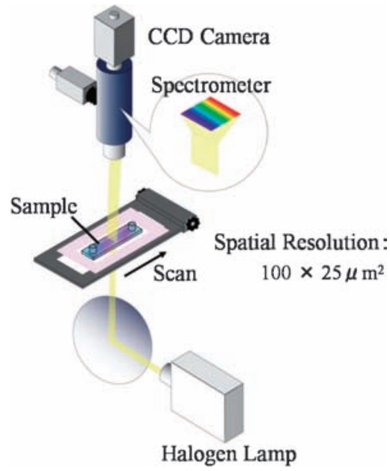

Figure 1. Schematic diagram of the imaging spectrometer in transmission geometry.

structure is fcc with a lattice constant of ca. 540 nm. The polycrystalline suspension was forced to flow in a flat capillary cell (gap height = 0.1 mm, width = 9 mm, and length = 70 mm) so that a shear-induced texture was formed in the cell. Two representative cases, i.e., weakly and highly sheared samples, were prepared for comparison. Figure 1 shows the schematic diagram of the imaging spectrometer (ImSpector, Kawasaki Steel Techno-research Corp., Chiba, Japan) in transmission geometry. White light from a halogen lamp was passed through the sample perpendicular to the cell surface and the light transmitted through the sample was detected using a charge-coupled-device detector with an in-plane image resolution of 100×25 microns. The transmission spectra in a wide sample area of $0.9 \times 3.2\,cm^2$ were collected by scanning the sample position; thus, the total number of pixels became 115,200.

As previously reported, the orientational regularity of sheared colloidal crystal in a flat capillary is highly dependent on the strength of shear flow. Figures 2a and 2b show RGB-composed images of the textures for two extreme cases—weakly and highly sheared samples—respectively. These are equivalent to color photographs under transmission illumination from a white lamp. From the appearances of these samples, it might be possible to infer that the optical quality of the weakly sheared sample is lower than that of the highly sheared one. However, it would be effective to use the statistical analysis of pixel-by-pixel spectra obtained by the imaging spectrometry to make the evaluation more quantitative.

Figures 2c and 2d are the superimposed transmission spectra from all the pixels for the two samples of Figures 2a and 2b, respectively. The portions in the figures with a light blue color indicate higher overlap. The dip at 840 nm is due to the Bragg

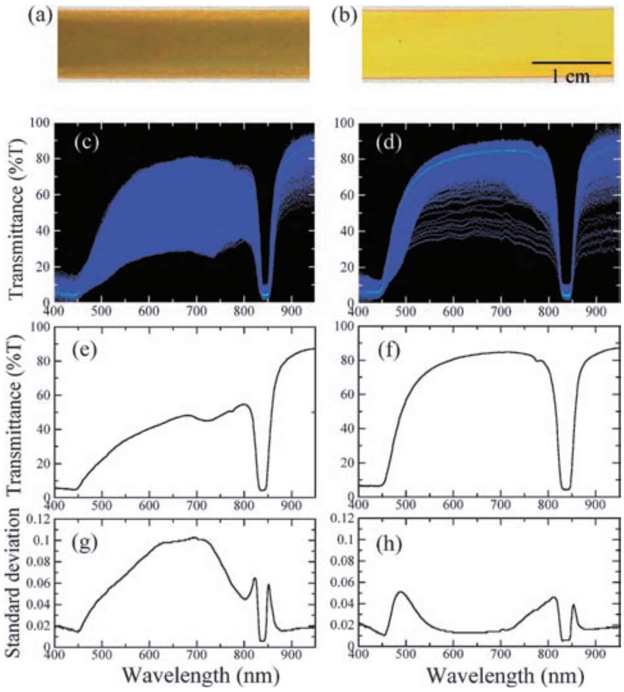

Figure 2. RGB images for (a) weakly and (b) highly sheared colloidal crystals under transmission illumination. Figures (c) and (d) show superimposed plots of pixel-by-pixel transmission spectra from all 115,200 pixels for (a) and (b), respectively. Figures (e) and (f) show average transmission spectra for (a) and (b), respectively. Figures (g) and (h) show standard-deviation spectra for (a) and (b), respectively.

diffraction from the (111) lattice planes of the fcc structure parallel to the cell surface. The transmission spectra for the weakly sheared sample were widely distributed in the wavelength region shorter than the (111) dip in comparison with the highly sheared sample. The average transmittance spectra were calculated (Figures 2e and 2f) using these spectral data for all pixels. Comparing the average spectrum for two cases, only the transmittance in the wavelength region that is shorter than the dip wavelength is significantly different, i.e., lower transmittance for the weakly sheared sample. Considering the Bragg conditions of the fcc lattice, the longest Bragg wavelength occurs when the incident light is normal to the {111} planes, which corresponds to the dip observed at 840 nm. If a sample includes polycrystalline portions with random orientations, various Bragg diffractions can occur at wavelengths shorter than the dip; this reduces transmittance. Therefore, the averaged transmission spectrum could be used to evaluate a degree of orientational regularity in a global sense.

On the other hand, in order to evaluate the spatial uniformity of the spectral characteristics, the standard deviation should be used instead of the average values. Figures 2g and 2h show the standard deviations of the transmittance (the standard-deviation spectrum) calculated from the pixel-by-pixel spectra for the entire area shown in Figures 2a and 2b, respectively. As in the case of the averaged spectrum, a significant difference between the two standard-deviation spectra appears in the wavelength region shorter than the dip. Thus, the weakly sheared sample has low quality not only in terms of the averaged optical characteristic but also the spatial uniformity, particularly at the pass-band region with shorter wavelengths than the (111) dip. It is noteworthy that the standard deviations for the weakly sheared sample are higher by almost one order of magnitude than those for the highly sheared one in the wavelength region between 600 and 700 nm. The standard deviation is inherently a good quantitative measure for evaluating fluctuation in physical quantities in general; however, the present results imply that the standard-deviation spectrum can be particularly useful for the evaluation of large-area colloidal crystals.

In summary, the spectral uniformity of large colloidal crystals can be evaluated by the imaging spectroscopy in transmission geometry. We have found that the spatial uniformity of the flow-aligned textures of colloidal crystals was quantitatively characterized by the standard deviation of transmittance at the pass-band wavelength. Spectral uniformity is an important factor for the application of colloidal crystals as optical devices; therefore, the present method can contribute significantly to progress in this field.

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