LAAN-A-UV-E059

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Application News

No. A553

Spectrophotometric Analysis

Evaluation of Photonic Materials with Biomimetic Structural Coloration

Colors occur either as pigments that absorb certain colors while reflecting/scattering others or as structural coloration caused by microscopic structures. Many living things in the natural world produce this type of structural coloration that results in vivid colors, including morpho butterflies, peacocks, and jewel beetles. Biomimetics is gaining attention as a field that utilizes the functions and structures of these living things in the development of new technology and manufacturing processes by mimicking them.

In Application News No. A502, we confirmed the existence of structural coloration on a multi-layered film produced by mimicking the wing structure of morpho butterflies, in which the coloration was caused by interference.[1)] The vivid colors observed on the wings of some birds are also structural coloration. For example, the structural coloration of peacock plumage is said to originate from the arrangement of melanin granules.[2)] Michinari Kohri, Associate Professor at the Division of Applied Chemistry and Biotechnology at Chiba University's Graduate School of Engineering, has succeeded in producing highly visible structural coloration by controlling the size, blackness, refractive index, and arrangement of melanin-mimicking particles (PSt@PSA particles) created by coating the surface of polystyrene particles (PSt) with polydopamine (PDA), which is similar to melanin.[3)]

This article introduces measurements of photonic materials with structural coloration performed in cooperation with Associate Professor Michinari Kohri.

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Spectrum and Color Value Measurement of Samples

Fig. 1 shows an image of the samples captured from above. The samples on the left side were formed only from PSt particles. The diameter of PSt particles becomes smaller moving from the top row of samples to the bottom row. The samples down the center were thinly coated with PDA (iridescent) and the samples on the right side were thickly coated with PDA (non-iridescent). Differences in PSt particle diameter and PDA coating thickness change the colors that are visible. Fig. 2 shows an image of the samples captured at an angle. The color tone of the samples changes according to the viewing angle. Fig. 3 shows a conceptual diagram of a melanin-mimicking particle.

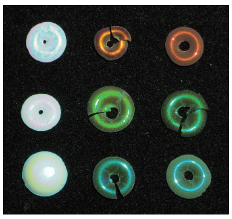

Fig. 1 Image of Samples Captured from Above

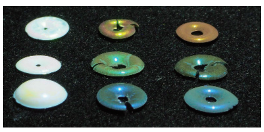

Fig. 2 Image of Samples Captured at an Angle

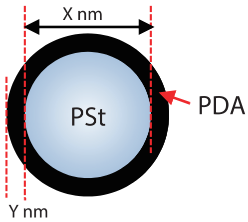

Fig. 3 Conceptual Diagram of a Melanin-Mimicking Particle
X: PSt Particle Diameter, Y: PDA Thickness

Fig. 4 shows inside the sample compartment of the SolidSpec-3700DUV with the variable angle absolute reflectance attachment installed. Use of the variable angle absolute reflectance attachment enables measurement with different angles of incident light with respect to the sample. For details on the variable angle absolute reflectance attachment, refer to Application News Nos. A390 and A394. Samples were set as shown in Fig. 4 and measurement was performed using the conditions listed in Table 1. Measurement was performed at incident angles of 5, 12, 30, and 45 degrees with the light beam reduced to a diameter of 1 mm by using the mask provided as an accessory with the SolidSpec-3700DUV.

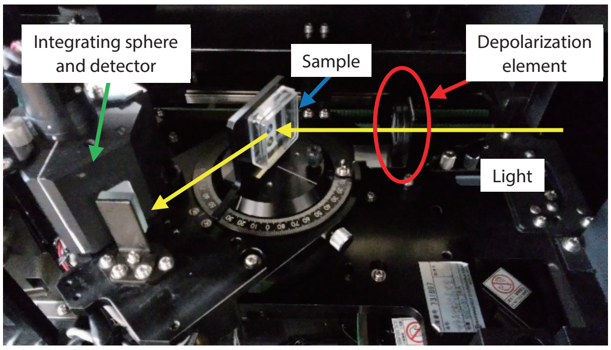

Fig. 4 Inside the Sample Compartment of the SolidSpec-3700DUV with the Variable Angle Absolute Reflectance Attachment Installed

Table 1 Measurement Conditions

Instrument	: SolidSpec-3700DUV, variable angle absolute reflectance attachment, quartz depolarizer *1
Measuring wavelength range	: 380 nm to 780 nm
Scan speed	: Low speed
Sampling interval	: 1.0 nm
Measurement light value	: Refractive index *2
Slit width	: 5 nm
	Light beam aperture mask ϕ1

*1: DEQ-2OP manufactured by SIGMAKOKI Co., Ltd. Produces artificially depolarized light.

*2: Since the refractive indices have mostly likely not been accurately measured due to the spherical shape of the samples, a.u. (arbitrary unit: unit for comparison as opposed to absolute values) was used as the reference value for the vertical axis.

Fig. 5 shows the reflectance spectra (5° incident angle) when the PSt particle diameter is constant and the PDA coating thickness is changed. We can see that a redshift occurs as the PDA thickness increases. Fig. 6 shows the color values calculated from the spectra plotted using commercially-available color analysis software. We can expect that as the PDA thickness increases, the color will shift from blue to green to yellow.

Fig. 7 shows the reflectance spectra (5° incident angle) when only the PSt particle diameter is changed. A redshift occurs as the PSt particle diameter increases. Fig. 8 shows the reflectance spectra (5° incident angle) when each PSt particle sample is thinly coated with PDA. These cases also show the occurrence of a redshift.

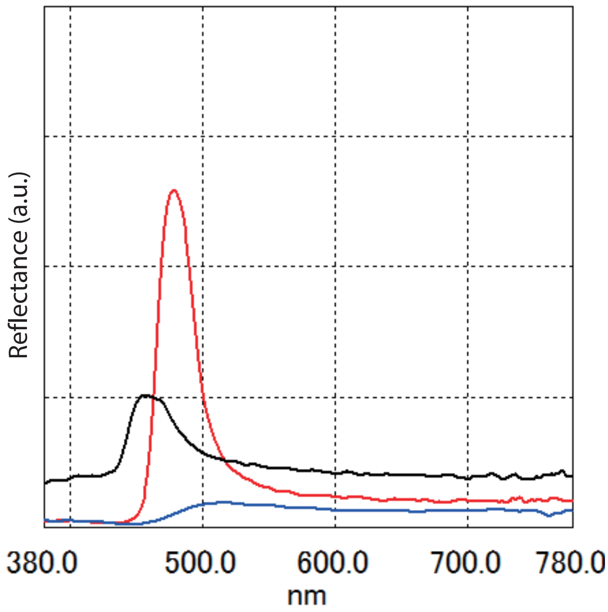

Fig. 5 Reflectance Spectra of Blue Coloring (5° Incident Angle)
Black: Uncoated PSt Particles,
Red: Thin PDA Coating (Iridescent),
Blue: Thick PDA Coating (Non-Iridescent)

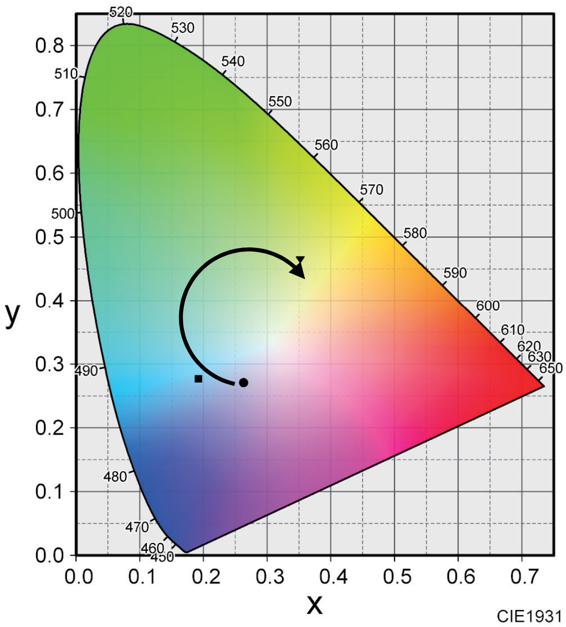

Fig. 6 Blue Coloring Color Values
Circle: Uncoated PSt Particles,
Square: Thin PDA Coating (Iridescent),
Triangle: Thick PDA Coating (Non-Iridescent)

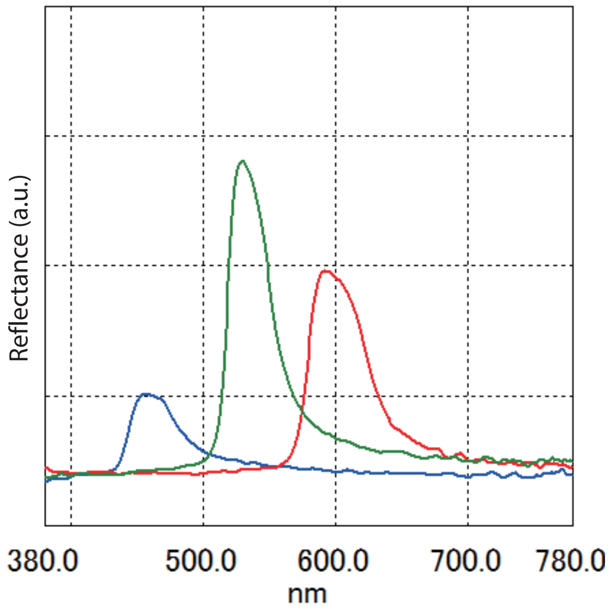

Fig. 7 Reflectance Spectra of PSt Particles with Differing Diameters (5° Incident Angle)
Blue: Blue Coloring (Uncoated PSt Particles),
Green: Green Coloring (Uncoated PSt Particles),
Red: Red Coloring (Uncoated PSt Particles)

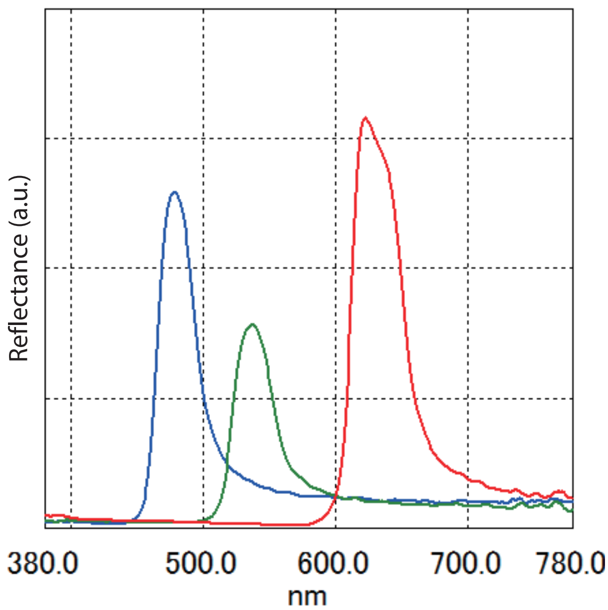

Fig. 8 Reflectance Spectra of PSt@PDA Particles with Thin PDA Coating (5° Incident Angle)
Blue: Blue Coloring (PSt@PDA Particles, Iridescent),
Green: Green Coloring (PSt@PDA Particles, Iridescent),
Red: Red Coloring (PSt@PDA Particles, Iridescent)

Fig. 9 shows the color values calculated from the spectra in Fig. 7 and Fig. 8 plotted using commercially-available color analysis software. This shows that the samples with PSt particles thinly coated with PDA exhibit a brighter color tone. Table 2 lists the color values and peak wavelength results.

Fig. 10 to Fig. 12 show the reflectance spectra resulting from light of differing incident angles striking the PSt@PDA particles thinly coated with PDA. A blueshift occurs as the incident angle increases for all of the samples. This is thought to be caused by incident angle differences in Bragg reflections.

Table 2 Color Values and Peak Wavelengths (5° Incident Angle)

Sample	x	y	Peak (nm)
Blue coloring (uncoated PSt particles)	0.263	0.271	454
Blue coloring (PSt@PDA particles, iridescent)	0.192	0.277	478
Blue coloring (PSt@PDA particles, non-iridescent)	0.352	0.466	517
Green coloring (uncoated PSt particles)	0.304	0.508	530
Red coloring (uncoated PSt particles)	0.447	0.359	593
Green coloring (PSt@PDA particles, iridescent)	0.323	0.612	536
Red coloring (PSt@PDA particles, iridescent)	0.647	0.298	624

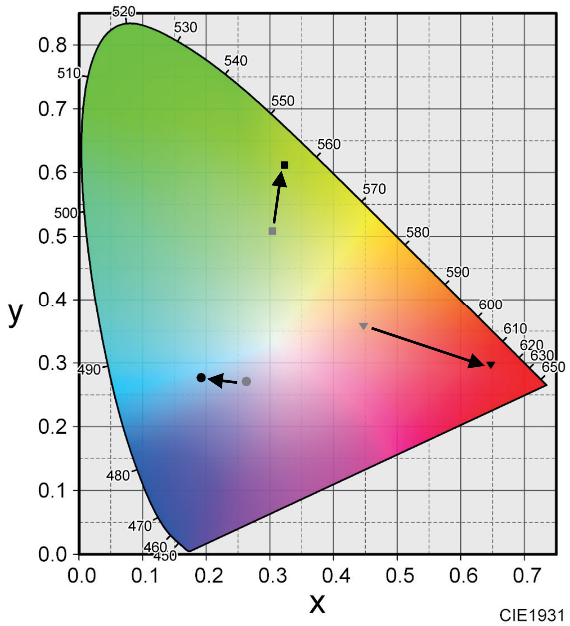

Fig. 9 Color Value Variation of Uncoated PSt Particles and PSt@PDA Particles (Iridescent)
Gray: Uncoated PSt Particles, Black: PSt@PDA Particles

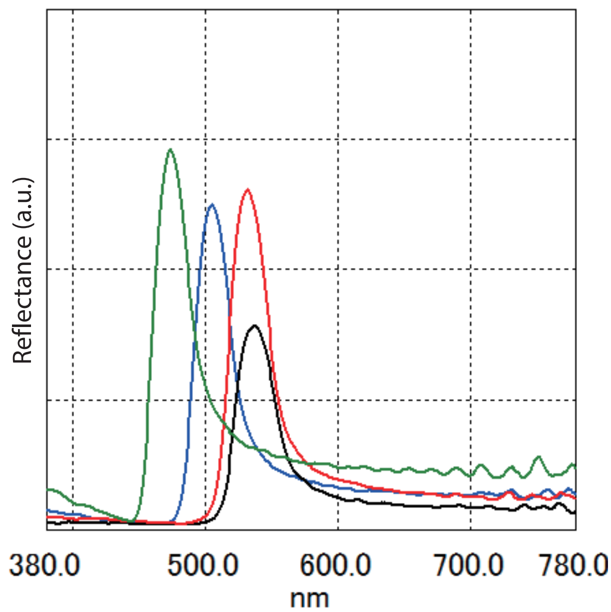

Fig. 11 Reflectance Spectra of Green Coloring (PSt@PDA, Iridescent)
Black: 5°, Red: 12°, Blue: 30°, Green: 45°

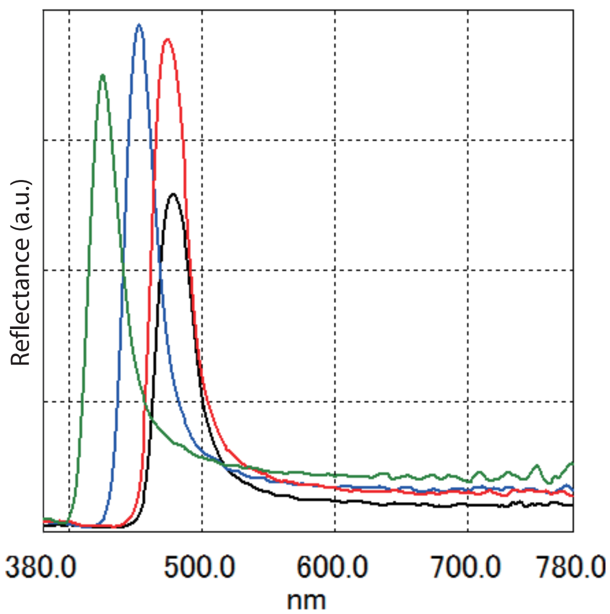

Fig. 10 Reflectance Spectra of Blue Coloring (PSt@PDA, Iridescent)
Black: 5°, Red: 12°, Blue: 30°, Green: 45°

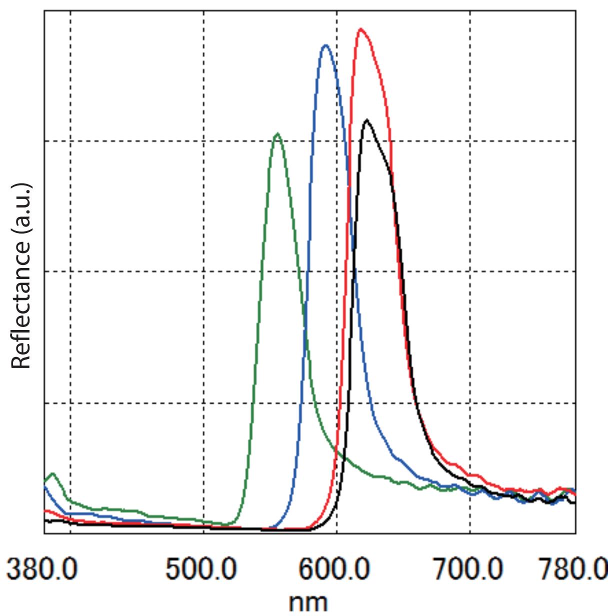

Fig. 12 Reflectance Spectra of Red Coloring (PSt@PDA, Iridescent)
Black: 5°, Red: 12°, Blue: 30°, Green: 45°

Observation of Particle Arrangement

Fig. 13 shows the SFT-4500 Nano Search Microscope that combines a laser microscope (LSM) and scanning probe microscope (SPM) to achieve high accuracy. The optical microscope and laser microscope were used to determine the observation position and the probe microscope was used to observe the arrangement of the green coloring particles. Fig. 14 to Fig. 16 show the 2D height images. The scanning range is 5.00 µm × 5.00 µm and the z range of the images is 300 nm. Fig. 14 and Fig. 15 show that the uncoated PSt particle sample and sample with a thin PDA coating have a regular arrangement of particles (colloidal crystal), whereas Fig. 16 shows that the sample with a thick PDA coating has an irregular arrangement of particles (amorphous structure). This difference in arrangement is considered to cause the differences in angular dependence and refractive index in the structural coloration of the samples.

Fig. 13 SFT-4500 Appearance

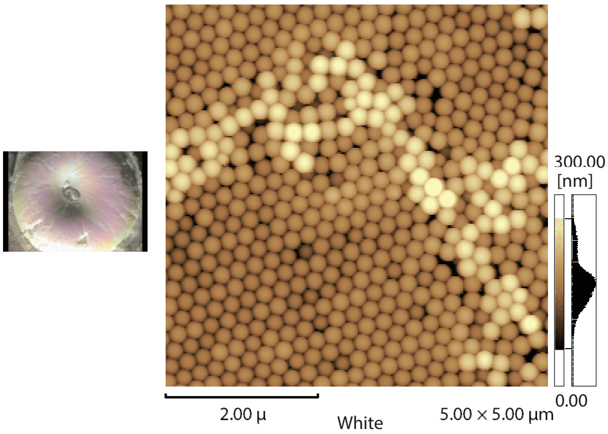

Fig. 14 Particle Arrangement of Green Coloring (Uncoated PSt Particles)

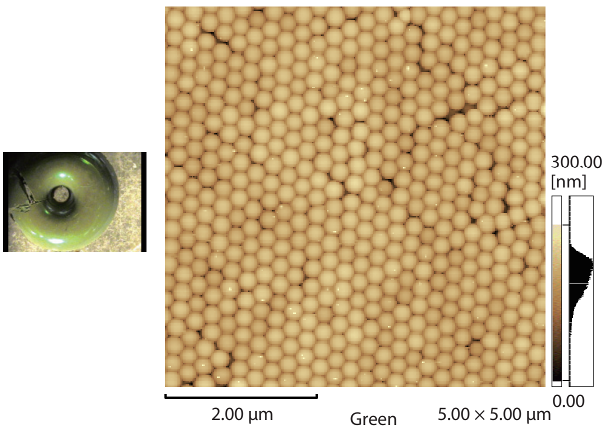

Fig. 15 Particle Arrangement of Green Coloring (PSt@PDA Particles, Iridescent)

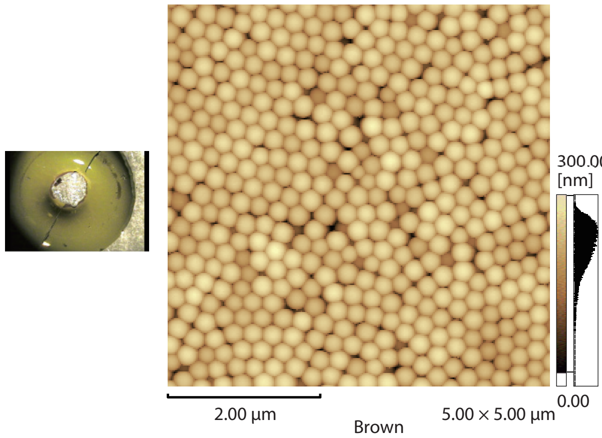

Fig. 16 Particle Arrangement of Green Coloring (PSt@PDA Particles, Non-Iridescent)

Conclusion

We conducted evaluation and observation of photonic materials with structural coloration using a spectrometer and the Nano Search Microscope. Using the spectrometer, we confirmed a shift in peak wavelength in the reflectance spectra that occurs according to the diameter of the PSt particles and the PDA coating thickness. We also confirmed a shift in peak wavelength in the reflectance spectra that occurs by changing the incident angle of light. Using the Nano Search Microscope, we confirmed a variation in particle arrangement that depends on the PDA coating thickness.

Since the color tone and angular dependence of structural coloration can be changed by controlling the size, blackness, refractive index, and arrangement of melanin-mimicking particles, it is expected this will lead to the development of ink materials with new types of color. The field of biomimetics is anticipated to allow manufacturing of efficient and environmentally-friendly materials such as these.

<Acknowledgments>
We would like to thank Associate Professor Michinari Kohri of the Division of Applied Chemistry and Biotechnology at Chiba University's Graduate School of Engineering for providing the samples used in these measurements and knowledge regarding biomimetics.

<References>

1) Shimadzu Corporation website
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2) Yoshioka, S. & Kinoshita S, Effect of Macroscopic Structure in Iridescent Color of the Peacock Feathers, Forma, **17**, 169 (2002)
3) Kawamura, A., Kohri, M., Morimoto, G., Nannichi, Y., Taniguchi, T. & Kishikawa, K. Full-Color Biomimetics Photonic Materials with Iridescent and Non-Iridescent Structural Colors, Sci. Rep. **6**, 33984 (2016)

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