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Optical Characterization of the Monodisperse Particle Multilayer with Coherent Structure

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Monodisperse polystyrene particle multilayer with coherent structure was constructed by Langmuir-Blodgett method. We have demonstrated that the particle multilayer was formed in face-center-cubic (FCC) structure. In addition, it was suggested that the introduction of nickel ion on the surface of particle would enhance the refractive index. The particle multilayers including other metal ions were prepared and the optical properties were characterized by reflectance spectrum. As a result, it was shown that the optical character of the particle multilayer was influenced by included concentration and refractive index of metal ion on the particle. Moreover, the particle multilayer, which was formed in FCC structure, showed the polarization-independency, even metal ion was included.
Key words: Optical Characterization, Monodisperse Particle Multilayer, Refractive Index, FCC Structure, Polarization-Independency

1. INTRODUCTION

Recently, the development of optical technology is finding wide uses in optical communication, sensor-technology, spectroscopy and medical appliance. These optical technologies could be an efficient communication tool by further advancement of hyperfine technology and application of wavelength division multiplexing (WDM). However, it is a serious obstacle that the polarization state makes the amplitude energy and modulation of optical signal lost. Further, control of refractive index of the optical device is another challenge for the application of the optical technology. Therefore, it is necessary to improve the polarization-independent component with an ability to control the refractive index for the development of optical elements and photonic devices[1,2].

Previously, we have constructed monodisperse polystyrene (PS) particle multilayer by Langmuir-Blodgett (LB) method. It was suggested that this particle multilayer was composed by face-center-cubic (FCC) structure, and thus showed coherent nature[3]. Since optical character of the particle multilayer depended on diameter and refractive index of the particle, inclusion of metal ion in the particle was one of the most efficient ways to increase the refractive index of the PS particle multilayer. Then, the sulfonated PS particle was prepared as a metal ion loadable particle. As a result, the refractive index of the particle multilayer was actually increased by the inclusion of nickel ion. The refractive index of the particle multilayer was varied by the content of nickel ion. It was suggested that the refractive index of the particle multilayer could be controlled by loading amount and kind of metal ion. In this study, inclusion of other metal ions, such as Ni^{2+}, Fe^{2+}, and Cr^{3+} in the particle multilayer was investigated. In addition, the polarization-independency of the particle multilayer was estimated by the reflectance spectrum.

2. EXPERIMENTAL

2.1 Materials

Monodisperse PS spherical particle (D=300 nm, Seradyn, Inc) was dialyzed with Milli-Q water for 2 days prior to use. The sulfonated PS particle was synthesized by using this monodisperse PS particle and chlorosulfonic acid in *n*-propanol at room temperature for 5 hours. And the obtained particles were agitated in NaOH aqueous solution (1 N) at 70 ℃ for an hour. The content of the sulfonated residues on PS particle was estimated to be 5.3 % of the total residues in the particle by ^{1}H-NMR measurement.

2.2 Deposition of particle layers

As a typical procedure: the PS particles and the sulfonated PS particles were dispersed in a mixed solvent of ethanol and *n*-butanol (1:1). The dispersion was gently added drop way on the surface of an aqueous media in Teflon trough using a micro-syringe. The spread particles were allowed to stand on the water surface for an hour, and then surface compression was carried out at a speed of 5 mm/min by LB film deposition apparatus (NL-BIO40s-MWC, Nippon Laser and Electronics Lab.). During the compressing, the surface pressure was measured by Wilhelmy plate. And the PS particle monolayer was transferred onto the hydrophobic silicon wafer. The particle multilayer was prepared by repeating the same process. The sulfonated PS particle layer was immersed into metal chloride aqueous solution. Then, this particle layer with metal ion was washed. Metal chlorides such as $NiCl_2$, $FeCl_2$ and $CrCl_3$, were used.

2.3 Measurements of reflectance spectrum

Reflectance spectrum measurements were performed by use of a UV-Vis spectrophotometer V-550 (JASCO) together with an attachment, ARV-474 (JASCO) with incident angles with 5 degree intervals of 5 to 50 degree. Optical character of the particle multilayer was estimated from reflectance spectra with incident angle from 5 to 50 degree by Bragg's law[4-6].

The polarized properties on the particle and the sulfonated particle multilayers were estimated from a horizontal polarized light (s-polarization) and a vertical polarized light (p-polarization) through the polarizer at several incident angles.

2.4 Measurement of concentration of including metal ion by DDTC method

The relation between the increasing of refractive index and complex amounts of metal ion was examined. The metal ions were determined from UV-Vis absorption spectrum using a sodium diethyldithiocarbonate (DDTC) as a chelating agent. About 1 mg of sulfonated PS particle in ethanol and 2 ml of metal chloride aqueous solution (5.0×10^{-4} M) were mixed and centrifuged. Subsequently, enough amount of DDTC aqueous solution was added in the supernatant. Amount of free metal ion was estimated by absorption at UV-Vis spectrum. Absorption wavelength of nickel ion (Ni^{2+}), ferrous ion (Fe^{2+}) and chrome ion (Cr^{3+}) were 433 nm, 505 nm and 505 nm, respectively. Amount of included metal ion, which was included with sulfonated PS particle, was calculated by subtraction of free metal ion amount in the supernatant from initial metal ion amount.

3. RESULTS AND DISCUSSION

3.1 Optical character of the particle multilayer including metal ion

In order to increase a refractive index of polymer, introduction of metal ion is one of the effective methods[7]. The including of Ni^{2+}, Fe^{2+} and Cr^{3+} onto the sulfonated PS particle multilayer was investigated. After immersing to corresponding metal chloride aqueous solution, reflectance spectrum of the particle multilayer was measured at 5 degree of incident angle

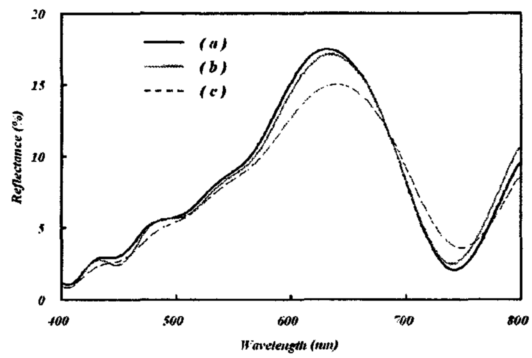

Fig.1 Reflectance spectra of the particle multilayer (5 layers) with metal ions ; (a) Fe^{2+}, (b) Ni^{2+} and (c) Cr^{3+}.

Table I The optical character of the particle multilayer with several metal ions.

	Peak wavelength (nm)	Refractive index of particle with metal ion
Ni^{2+}	634	1.62
Fe^{2+}	633	1.62
Cr^{3+}	644	1.64

(Fig.1). Typical spectra attributed to interference of multilayer were observed. Wavelength of the maximum peak of each reflectance spectra were observed at 634 nm, 633 nm, and 644 nm for Ni^{2+}, Fe^{2+}, and Cr^{3+}, respectively (Table I). Comparing with the maximum peak of the PS multilayer (624 nm), the observed maximum peaks shifted to higher wavelength by 10 nm, 9 nm, and 20 nm, respectively. In addition, when the PS particle multilayer was soaked in metal chloride aqueous solution, no shift was observed in the reflectance spectrum. It was suggested that inclusion of metal ion in the sulfonated PS particle did not occur by adsorption or trapping in the particle, but by ionic binding between metal ion and sulfonated group. Refractive index was calculated from the reflectance spectra of the multilayer with various incident angles together with Bragg's law. The obtained refractive indexes were actually larger than that of PS particle multilayer, 1.59 (Table I). It was suggested that inclusion of metal ion in the particle multilayer influenced to the optical character of the constructed multilayer.

The included amount of metal ion in the sulfonated PS particle multilayer was estimated by DDTC method (Table II). It was shown that the included amount of metal ion was very small, and 60-70 % of the sulfonated group on the PS particle were concerning to the inclusion of metal ions. That is, the included amount of metal ions could be regarded as same degree, but the contribution to enhancement of the refractive index was remarkable. It should be caused by the fact that multivalent cationic ion formed cross-linking

Table II The content of the metal ions on the sulfonated PS particle.

	Concentration of metal ion on the PS particle (μmol/mg)	The occupation share of sulfonated group on particle that corresponds to metal ion (%)
Ni^{2+}	0.170	67
Fe^{2+}	0.143	56
Cr^{3+}	0.107	66

with the sulfonated group on the PS particle, and then dense part should be formed in the PS particle surface. Density of the particle layer directly affect to the refractive index. Thus, the dense part in the PS particle made the refractive index of the particle multilayer high. This speculation was supported by the fact that enhancement of the refractive index by trivalent cationic ion, Cr^{3+}, was higher than divalent cationic ion, such as Ni^{2+} and Fe^{2+}.

3.2 Polarization-independency of the particle multilayer

The polarized reflectance spectra of the PS particle multilayer at 45 degree of the incident angle were shown in Fig.2A. The maximum and minimum peaks of the polarized spectra were almost agreed with those of spectrum with natural light. These results suggested that the constructed multilayer was actually independent to s-/p-polarized light, i.e. polarization-independent. In the reflectance spectra of the sulfonated PS particle multilayer with Ni^{2+}, the maximum and minimum peaks of the polarized spectra showed no shift from the natural light (Fig.2B). It was suggested that the PS particle multilayer with Ni^{2+} retained the polarization-independency, even though metal ion formed cross-linking in the PS particle to cause a localization of density. The particle multilayer with and without metal ion showed FCC structure[3]. Thus, it should be considered that introduction of multivalent metal ion in the PS particle affected to the micro-environment such as density in the particle, but did not affect to macro-environment such as FCC structure of the particle multilayer.

4. CONCLUSION

Multilayer constructed by the sulfonated PS particle was successfully applied to include metal ions. Inclusion of multivalent metal ion caused enhancement of the refractive index of the particle multilayer. This result should be attributed to the fact that density of the particle increased by cross-linking with the multivalent metal ion and sulfonated group. Regardless of the increasing of the density inside of the PS particle, the multilayer showed "polarization-independency". Thus, the multilayer of the sulfonated PS particle with FCC structure would be applied for optical device with controllable refractive index and polarization-independent property.

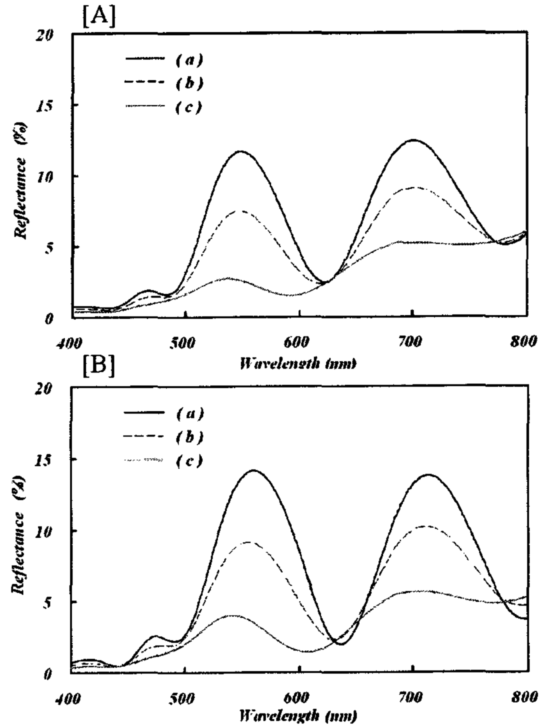

Fig.2 Reflectance spectra of the PS particle multilayer [A] and the particle multilayer with Ni^{2+} [B] at incident angle of 45 degree; (a) s-polarized light, (b) natural light and (c) p-polarized light.

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