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# Preparation and Fluorescent Properties of Rhodamine B–hexadecylamine-intercalated Graphite Oxide Thin Film

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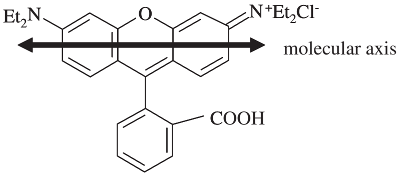
Thin film samples of Rhodamine B–hexadecylamine-intercalated graphite oxides were prepared by cast method from chlorofolm solution of Rhodamine B and hexadecylamine-intercalated graphite oxide. The emission maxima red-shifted with increasing Rhodamine B content in the sample. The tilted alkylamine may prevent the formation of nonfluorescent Rhodamine B H-dimer.

Recently, solid-state materials with light emitting ability are desired in order to replace dye laser using solution which requires complicated equipments such as a large circulator. In this context, many solid host materials such as porous silica gel, polymer, dye-cored dendrimer, etc. have been considered and fluorescent properties of dye molecules in them has been investigated.[1–7] Layered materials containing dye molecules in their 2-D space are one of the candidates for the host materials. However, when dye molecules are introduced into clay minerals, they tend to form nonfluorescent aggregates.[1] In order to overcome this problem, very recently, Sasai, et al.[2] have shown that Rhodamine 6G/cationic surfactant/clay hybrid, in which the surfactant prevents aggregation of the dye, emits light with appropriate surfactant/dye ratio. These hybrid materials, however, were obtained as powder form which is not available for light emitting or laser devices as they pointed out. In this study, therefore, we introduce hexadecylamine-intercalated graphite oxide[8] as the host of dye molecules. This material is well-dispersed in organic solvent such as chlorofolm, which makes it easy to prepare thin film samples by the cast or spin coating methods. Rhodamine B molecules were intercalated into hexadecylamine-intercalated graphite oxide with various dye contents and fluorescent properties were investigated.

Graphite oxide ($C_8O_{3.4}H_{2.3}$; GO) was obtained from natural graphite powder (57/74 μm) by the Brodie's method.[8] Intercalation of hexadecylamine ($C_{16}H_{33}NH_2$; C16) was performed by mixing GO and C16 in the pestle in the presence of a small amount of hexane (C16/GO ratio of 0.6) and the resulting sample was dried at 60 °C overnight.[8] Intercalation of Rhodamine B (RhB) was performed by cast method[2] from $CHCl_3$ solution of intercalation compound (3.3 mM) and organic molecules (0.93 mM). Scanning electron microscope observation of the obtained transparent films (thickness: 0.5/0.9 μm) indicated that GO layer was parallel to the substrate. The ratio of RhB/GO varied between 0.01 and 1. These samples were analyzed by X-ray diffraction (Rigaku Rint-2100, Cu K$\alpha$ radiation), UV–vis (Hitachi U-3010) and fluorescence (Hitachi, F-2500, excitation wavelength; 420 nm) measurements. The angle of RhB against GO layer was determined based on the polarized UV spectroscopy, using a film polarizer. The tilt angle; $\gamma$ of the molecular axis of RhB (indicated by an arrow in Scheme 1) against GO layer for the sample with RhB/GO ratio of 0.01 and 0.5 was calculated from dichroic ratio; R at 560.5 or 563.5 nm using the following equation as in the literature.[1]

$$\mathrm{R} = [2\sin^2\alpha - (3\sin^2\alpha - 1)\sin^2\gamma]/\sin^2\gamma \qquad (1)$$

Here, $\alpha$ is the incident angle of the polarized light and for the angle of the molecular axis to the optical transition moment of 0° was used.



**Scheme 1.** Molecular structure of Rhodamine B.

Figure 1 shows the X-ray diffraction patterns of $(C16)_{0.6}GO$ and RhB-intercalated $(C16)_{0.6}GO$. A diffraction peak was observed at $2\theta = 3.2°$ (interlayer spacing; $I_c = 2.73$ nm), indicating layered structure. This peak became broad and shifted to $2\theta = 3.0°$ ($I_c = 2.94$ nm), when the RhB contents were higher than 0.2 per GO unit. These suggest that RhB molecules were intercalated into $(C16)_{0.6}GO$.

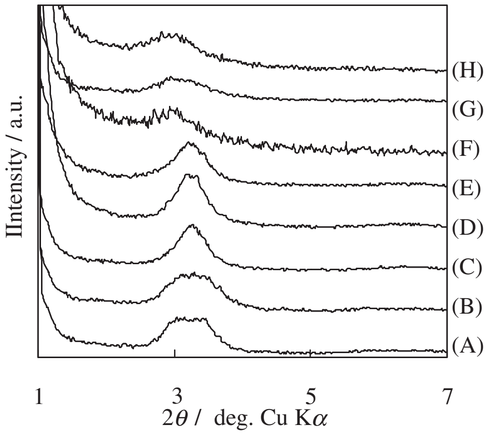


**Figure 1.** X-ray diffraction patterns of (A): $(C16)_{0.6}GO$ and $(C16)_{0.6}GO$ with various RhB/GO ratios. (B): 0.01, (C): 0.025, (D): 0.05, (E): 0.1, (F): 0.2, (G): 0.5, and (H): 1.

Assuming that C16 molecules take bilayer structure without interdigitation, the tilt angles of alkyl chains are calculated to be 27.3° and 30.4°, respectively. Here, we used 0.6 nm for the thickness of GO and 2.31 nm ($0.127 \times 16 + 0.28$ nm) for the length of C16 with all trans orientation of alkyl chains.

Figures 2 and 3 show the absorption and fluorescence spectra of RhB intercalated $(C16)_{0.6}GO$. The peak shape of the absorption around 560 nm was very similar to that observed in a dilute solution of RhB, when the RhB/GO ratio was low, suggesting that RhB molecules were monomerically introduced into $(C16)_{0.6}GO$. The absorption peak shifted to longer wavelength and the shoulder at 515 nm was more clearly observed for the sample with RhB/GO ratio higher than 0.2. The absorption spectrum of $(C16)_{0.6}GO$ with RhB/GO = 1 showing two broad peaks at 574 and 520 nm was rather similar to that of neat RhB cast film from chlorofolm solution.

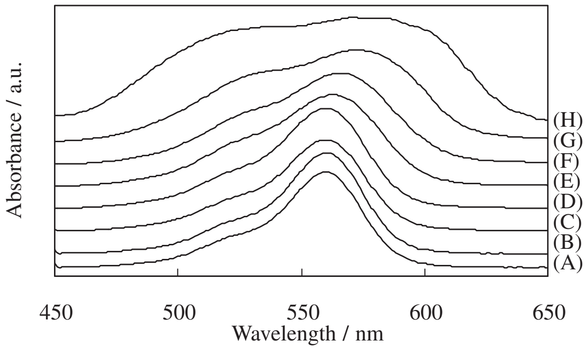


**Figure 2.** UV–vis spectra of $(C16)_{0.6}GO$ with various RhB/GO ratios. (A): 0.01, (B): 0.025, (C): 0.05, (D): 0.1, (E): 0.2, (F): 0.5, (G): 1 and (H): neat RhB.

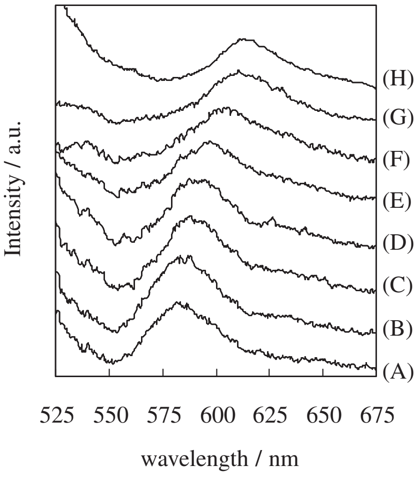


**Figure 3.** Fluorescent spectra of $(C16)_{0.6}GO$ containing various amounts of RhB. (A): 0.01, (B): 0.025, (C): 0.05, (D): 0.1, (E): 0.2, (F): 0.5, (G): 1, and (H): neat RhB.

On the other hand, in fluorescent spectra, an emission peak at 582 nm was observed for the sample with RhB/GO ratios less than 0.025 (Figures 3a and 3b), which was close to that of RhB monomer. This emission maximum shifted to higher wavelength from 582 to 614 nm with increasing RhB content. The latter wavelength observed for $(C16)_{0.6}GO$ with RhB/GO = 1 was similar to that observed for neat RhB cast film as shown in Figure 3h. It has been reported that the absorption peak at 520 nm and emission at 610/625 nm mean the formation of fluorescent RhB J-dimer with the angle between the molecular axis of two RhB molecules less than 55°.[4,9] These facts clearly indicate that RhB molecules are monomerically intercalated into $(C16)_{0.6}GO$ with lower RhB/GO (0.025) and form J-dimers with higher RhB contents.

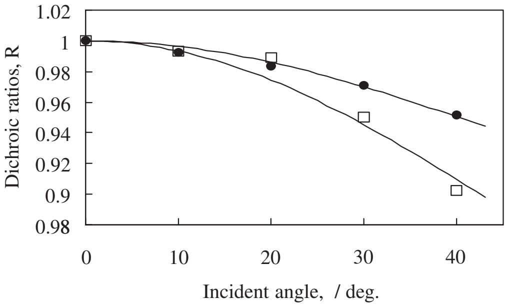


**Figure 4.** Dichroic ratio for the absorption of RhB as a function of incident angle. □: RhB/GO=0.01 and ●: RhB/GO=0.5 The solids line were determined in accordance with Eq 1.

Figure 4 shows the dichroic ratio of $(C16)_{0.6}GO$ with RhB/GO = 0.01 and 0.5 at 560.5 and 563 nm, respectively as a function of incident angle. When the above data were well fitted with Eq 1 as show by the solid lines in Figure 4, and the angle $\gamma$ was determined to be 58.0° and 56.4° for $(C16)_{0.6}GO$ with RhB/GO = 0.01 and 0.5, respectively. The angle was then evaluated to be 32.0° and 33.6° as the angle between the molecular axis and GO layer. These values were very close to those of alkyl chains determined from the X-ray diffraction data and were consistent with the formation of J-dimer. In addition, tilted alkylamine might prevent the formation of nonfluorescent H-dimer.

Finally, the results obtained in this study indicate that alkylamine-intercalated graphite oxide is a promising host material for dye molecules such as RhB and is applicable for tunable solid laser.

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