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THIRD-ORDER NONLINEAR OPTICAL PROPERTIES OF CYANINE DYES ADSORBED ON SMALL METAL PARTICLES

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Abstract We prepared dispersions of composite particles of thiacarbocyanine dye and colloidal silver or gold and examined an effect of the composite on the third-order nonlinear susceptibility ($\chi^{(3)}$) measured by using degenerate four-wave mixing method. The $\chi^{(3)}$ of the dispersion was enhanced about 3.5 times the sum of those of dye solution and colloidal metal dispersion. A new absorption band (λ=600 nm) which was bathochromically shifted from monomer band (λ=551 nm) was formed and this band was related to the enhancement of $\chi^{(3)}$.

INTRODCTION

It has been known that colloidal silver and gold dispersions have large third-order nonlinear susceptibility ($\chi^{(3)}$).[1,2] On the other hand, in the field of nonlinear optics much attention has been paid on organic dyes because of their large $\chi^{(3)}$ values. In particular, cyanine dyes and their aggregates were investigated by many researchers and the influences of aggregation of the dyes on the nonlinear optical properties have been interesting research subjects.[3-5] In this study, we examined an effect of composite on $\chi^{(3)}$ of dispersions of noble metal particles adsorbing cyanine dye.

EXPERIMENTAL SECTION

5,5'-dichloro-3,3',9-triethylthiacarbocyanine chloride (Thia; Figure 1) was purchased from Japanese Research Institute for Photosensitizing Dyes Co. and used without further purification. Colloidal silver or gold dispersions were prepared by photolysis of the aqueous solution containing 1 mM (1 M=1 mol dm^{-3}) $AgClO_4$ or $HAuCl_4$, 35 mM sodium dodecyl sulfate (SDS) and 100 mM acetone[6]. SDS and acetone were removed

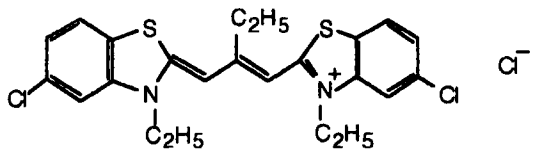

FIGURE 1 Chemical structure of Thia.

from the dispersion by dialysis. Dispersions of composite particles of Thia and the noble metal were prepared by adding the aqueous solution of Thia to the colloidal metal dispersions. Extinction spectra of the dispersions were measured by the Shimadzu spectrophotometer UV-260.

The $\chi^{(3)}$ values of the dispersions were measured by a phase conjugated degenerate four-wave mixing arrangement[7]. A frequency-doubled Nd:YAG laser (λ=532 nm, Quantel International, YG571C) was used as the light source. The pulse duration and the intensity were 7 ns and 0.9 MW cm^{-2}, respectively. The sample dispersion was put in the quartz cell of 1 mm in thickness. Both the phase conjugate reflection beam and the reference beam of the probe were detected by a streak camera (Hamamatsu Photonics, Temporal photometer C1587). The $\chi^{(3)}$ values of the dispersions were calculated by the following equation using the reflectivity for CS_2 as a standard.

$$\chi^{(3)}_{\text{Sample}} = Q\left(\frac{n_{\text{Sample}}}{n_{CS_2}}\right)\sqrt{\frac{R_{\text{Sample}}}{R_{CS_2}}}\,\frac{I_{CS_2}}{I_{\text{Sample}}}\,\chi^{(3)}_{CS_2}$$

Here, n, R and I are the refractive index, the conjugate reflectivity and the pump beam power, respectively. $\chi^{(3)}$ value of CS_2 was assumed to be 1.7 pesu.[8] Q denotes the correction factor for the light absorption by the sample, represented by $\ln(1/T)/[\sqrt{T}(1-T)]$, where T is the transmittance of the sample at 532 nm. In order to investigate the response time of the $\chi^{(3)}$, variation of phase conjugated reflectivities with delayed backward pump light was also measured using 40 ps pulses with 50 MW cm^{-2} power.

RESULTS AND DISCUSSION

Figure 2 shows the variation of the $\chi^{(3)}$ of the dispersion of composite particles of Thia and colloidal silver with the concentration of silver, where concentration of Thia was fixed to 30 μM. $\chi^{(3)}$ of Thia solution without silver was 3.7 pesu. $\chi^{(3)}$ of colloidal silver was proportional to the concentration and 0.34 pesu per 100 μM silver. If there

was no composite effect, $\chi^{(3)}$ of the dispersion should increase slightly in proportion to the concentration of silver as indicated with the dotted line in Fig. 2. However, when the concentration of silver was 30- 60 μM, $\chi^{(3)}$ of the dispersion was larger than the simple sum of $\chi^{(3)}$ of dye solution and colloidal silver dispersion. The maximum value was 14 pesu at [Ag]=50 μM. When the concentration of silver was increased furthermore, $\chi^{(3)}$ was reduced steeply to the value of the simple sum. $\chi^{(3)}$ of the dispersion of composite particles of Thia and colloidal gold showed similar variation with concentration of gold. It is considered that $\chi^{(3)}$ of the dispersion can be enhanced in certain concentration of colloidal metal by the composite effect of Thia and noble metal particles.

The extinction spectra of the dispersions of composite particles of Thia and colloidal silver are shown in Figure 3. Here, concentration of Thia was 30 μM. The presence of silver particles resulted in the decrease of absorption bands of monomeric (λ=551 nm) and dimeric (λ=510 nm) Thia, while the broad band around these bands was characteristically observed. The broad spectra indicate the formation of several new bands due to adsorbed dye.[9] On the other hand, absorption band of colloidal silver was seen at λ=410 nm and the shape of the band was not influenced by mixing with Thia. Optical density at the wavelength of pulse laser (λ=532 nm) was almost independent of the concentration of silver. The broad extinction spectra of the dispersions can be separated into several bands; B_1(λ=600 nm), B_2(λ=578 nm), monomer, dimer,

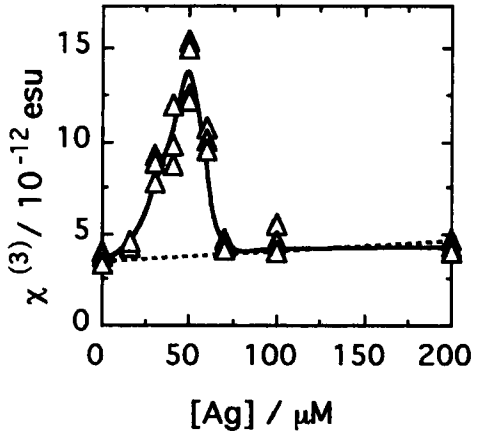

FIGURE 2 Variation of $\chi^{(3)}$ of dye solution with the concentration of silver colloid. The dotted line; simple sum of $\chi^{(3)}$ of dye solution and silver colloid.

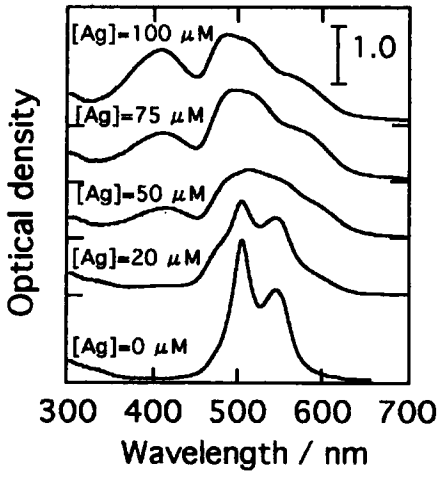

FIGURE 3 Extinction spectra of dye solution with silver colloid.

H_1(λ=485 nm) and H_2(λ=467 nm). These bathochromically (B_1 and B_2) and hypsochromically (H_1 and H_2) shifted bands correspond to aggregated dye with head-to-tail and face-to-face packing, respectively. B_2, H_1 and H_2 bands increase monotonically when the concentration of silver increases up to 60 μM and they remain almost constant at [Ag]$\geqq$60 μM. On the other hand, B_1-band increases with the concentration of silver at [Ag]$\leqq$50 μM and steeply decreases at [Ag]=50-70 μM. Extinction spectra of dispersions of composite particles of Thia and colloidal gold showed similar variation. For both colloidal silver and gold, the variation of B_1-band is similar to that of $\chi^{(3)}$. Therefore the formation of B_1-band is considered to contribute to enhancement of $\chi^{(3)}$.

The phase conjugated reflectivities of dispersions of composite particles of Thia and colloidal gold with the delayed backward pump light using 40 ps pulses increased at the delay time of 200 ps and 400 ps. These increases are not seen in dye solution and colloidal gold dispersion and are considered to be brought about by an additional thermal mechanism. This thermal mechanism is considered to contribute to the enhancement of $\chi^{(3)}$ measured by 7 ns pulses mentioned above. Quenching of dye luminescence was also observed in the dispersions. The quenching can be attributed to energy transfer from adsorbed dye to noble metal particles. The detail of the relationship of thermal mechanism and the variation of $\chi^{(3)}$ is now under investigation.

In summary, the $\chi^{(3)}$ values of the dispersions of composite particles of Thia and colloidal noble metal were increased at certain concentration range of noble metal. This increase well correlated with the appearance of the absorption band at 600 nm (B_1-band). The enhancement of $\chi^{(3)}$ is considered to be due to the formation of the thermal phase grating.

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