High nonlinear optical coefficient ($\chi^3 = 10^{-7}$ esu) of cyanine dye J aggregates doped silica film synthesized by a simple sol–gel method

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Abstract

We have synthesized, for the first time, a thin silica film doped with condensed J aggregates of 1,1'-diethyl-2,2'-cyanine bromide dye using a simple sol–gel method. The film is homogeneous in thickness and stable at room temperature. The J band formed in the spin coating process is independent of polarizer angle and the film is isotropic without any dichroism. The high optical nonlinearity ($\chi^3 = 5.0 \times 10^{-7}$ esu) of the film at the resonance wavelength ($\lambda = 577$ nm) of the J aggregates was first observed by Z-scan using a 180 fs pulse laser at 77 K under a vacuum ($< 10^{-5}$ torr). The doping ratio of J aggregates in silica film suggests that the net value of pure J aggregates is $4.0 \times 10^{-6}$ esu. Preliminary experiments using a pump-probe showed the film to have a response time $\tau$ of 0.5 ps under 575 nm excitation at room temperature. Since the J aggregates are incorporated into the silica film, further research is likely to lead to improved stability. © 2002 Published by Elsevier Science B.V.

Keywords: Nonlinear optical coefficient; J aggregates; Doped silica film

1. Introduction

Cyanine dyes have played an important role as photosensitizers for photography [1] and lithography [2]. Recent interest has focused on the potential employment of J aggregates of cyanine dyes in many applications, including non-linear optical devices [3,4], photoelectric cells [5,6] and multiple photo-recording devices [7]. J aggregate materials, if used in the above applications, need to satisfy the following requirements: (1) thin films are preferred for ease of handling, (2) they need to contain high concentrations of J aggregates, (3) processing should be simple, and (4) J aggregates must be stable. As a result, various synthesis processes, such as solutions [8], Langmuir–Blodgett (LB) films [9], crystals [10] and dispersed polymer films [11,12] have been investigated. However, process optimization is still needed to achieve further improvements [13].

Here, we report that, although PVA polymer film [11,12] and bulk silica materials [14] doped with monomers and J aggregates of cyanine dyes have already been described, thin silica films (about 150 nm) doped with high density J aggregates can be synthesized using a simple sol–gel method. In spite of containing a high density of J aggregates, these films are homogeneous and much more stable than LB films. The high optical nonlinearity ($\chi^3 = 5.0 \times 10^{-7}$ esu) of the film at the resonance wavelength ($\lambda = 577$ nm) of the J aggregates was first observed using Z-scanning employing a 180 fs pulse laser at 77 K under a vacuum ($< 10^{-5}$ torr). The doping ratio of J aggregates in silica film suggests that the net value of pure J aggregates is $4.0 \times 10^{-6}$ esu. Preliminary experiments using a pump-probe showed the film to have a response time $\tau$ of 0.5 ps under 575 nm excitation at room temperature. These films have potential for practical use in nonlinear optical switching devices.
2. Experimental

The cyanine dye employed in our experiment was 1,1'-dimethyl-2, 2'-quinocyanine bromide (NK-1046, Nippon Kanko–Shikiso Kenkyusho Co., Ltd., Japan). The structure is shown in Fig. 1(a). The dye was used without further purification.

The silica films doped with J aggregates of cyanine dyes were prepared in the following way: 0.25 ml tetraethyl orthosilicate (TEOS) was mixed with 5 ml ethanol (EtOH) and stirred for 10 min. The solution was added with 0.0725 ml HCl (0.14 N) and stirred for 60 min. This solution became the mother solution. It was added with different amounts of cyanine dye and stirred for another 180 min. Finally, the sol-solution was used for film deposition on quartz substrates (9.0 × 30 × 1.0 mm³) by spin coating in two steps: spinning at a low speed of 250 rpm for the initial 3 s followed by a high speed of rotation of 500–4000 rpm for a final 10 s. All of the film fabrication procedures were carried out at room temperature (28 °C). The procedure for preparation is summarized in Fig. 1.

The sol-solution of cyanine dyes was red but the dye-doped silica film was purple, indicating that J aggregates form during the spin-casting procedure. The film thickness and refractive index were evaluated by ellipsometry (Auto EL-III, Rudolph Research). The optical characteristics of the cyanine dye J aggregate silicate films were investigated by UV–VIS absorption spectroscopy (Hitachi U-4000) and fluorescence microscopy (Olympus BHMS). The third order nonlinear optical susceptibility of the film was measured by Z-scanning using 180 fs pulsed laser light. The decay spectra of bleaching at 575.00 nm and induced absorption changes at 569.2 nm were investigated using a femtosecond-pulse pump probe.

3. Results and discussion

Fig. 2(a) shows the absorption spectra of the sol-solution and the silica film; the dotted line shows the sol-solution and the solid line shows the spin-coated silica film. The sol-solution is red; the dye-doped silica film is purple, indicating that no cyanine dye molecules formed aggregates in the sol-solutions, whereas they formed J aggregates in the silica films. The band at 330 nm is assigned to the quinoline rings in the dye molecule structure. As shown in the dotted line, the bands around 495 and 530 nm result from the \( p \)-electron absorption band between the N atoms in cyanine dye molecules in monomeric condition. The solid line shows the spectrum of the silica film created from the sol solution by spin coating. A very sharp J band peak can be seen at 576 nm. In addition to the J band, there are the two sub-bands, one resulting from dimer (or H aggregate) bands, which are located at about 504 nm [15]; the other is the monomer band of the cyanine dye. Within the films, the monomers and the various aggregates are able to coexist, but the J aggregates predominate. The fluorescence spectrum of the spin coated silica film is shown in Fig. 2(b). The shift between the fluorescence and absorption spectra is only about 5 nm, which means that a characteristic small Stokes shift of J aggregates is observed.

Fig. 3(a) depicts the dependence of J band absorption of the J aggregates in the silica film on the cyanine dye concentration of the starting solution. The J band absorbance drastically increases with increased cyanine dye concentration in the range from 0.10 to 0.30 wt.% in the starting solution, and saturates at a dye concentration of over 0.30 wt.%.
The solution is dropped onto the substrate. Next, the formation process is regarded as taking place as follows. On the basis of the above results, the silica film formation process is regarded as taking place as follows.

**Fig. 3.** The J absorption band in the J aggregated doped silica film depends on (a) the dye concentration in the solution; (b) the 2nd step spin speed of film coating.

**Fig. 3(b)** shows the J aggregation absorbance band dependence on the 2nd step spin speed during the film coating from cyanine dye concentration at 0.33 wt.%. J aggregation tends to be promoted by increasing the spin speed. The promotion of J aggregation increases rapidly when spin speed is increased from 0 to 1000 rpm, saturating at speeds over 1000 rpm. Fluorescence microscopy revealed that the grains of the J aggregates were homogeneously dispersed in the silica matrix. The grain size was about 1 µm, and tended to decrease with increased spin speed. The uniformity and homogeneity of the films also depends on the speed of rotation. Whereas the films fabricated at low speeds below 1000 rpm showed fine cracks, lack of uniformity in thickness, and varying opacity; the films fabricated at speeds of 1000 rpm or above were of uniform thickness and crack-free. All the absorbance intensities in **Fig. 3** are normalized at the quinoline ring band of 330 nm.

On the basis of the above results, the silica film formation process is regarded as taking place as follows. First, the solution is dropped onto the substrate. Next, any excess solution is removed by spinning; the remainder forms a liquid film on the substrate. Its thickness is defined by the speed of rotation. At the same time, the sol solution is rapidly condensed by evaporation of EtOH from the liquid film. As a result, both the aggregation of the dye molecules and the condensation polymerization of TEOS compete in the film. The J aggregates of dyes are consequently incorporated in the SiO₂ framework on the substrate.

There are three principal reactions competing along the pathway from a sol-solution to a silica film: (1) evaporation of EtOH, (2) aggregation of dye molecules, and (3) condensation and polymerization of TEOS. These competitions depend on reaction factors such as the dye concentration in the sol-solution, the thickness of the liquid film on the substrate, the speed of rotation, temperature and pH. These factors consequently affect the dye aggregation conditions in the SiO₂ framework. The dependence of J aggregation on dye concentration can be explained in the following way: when a low concentration sol-solution is used in film fabrication, J aggregation is impeded in the silica film. This is because the condensation polymerization of TEOS becomes more dominant than dye aggregation, resulting in isolated dye molecules being confined in the SiO₂ framework. Furthermore, the spin coating speed dependence of the J aggregation can be interpreted in the following way: since a thin liquid film on the substrate dries more rapidly than a thick film, EtOH in thin liquid films is likely to evaporate to a greater extent than in thick films. Fast spinning of the substrate decreases the film thickness of the liquid film on the substrate. As a result, the rate of aggregation of the dye is much faster than that driven by simple polymerization of TEOS. Aggregation is thus promoted by fast spinning.

In our film fabrication, choice of solvent is important. In addition to compounds with affinity for water and alkoxysilane, such as TEOS, solvents in which the dyes are highly soluble must be employed: if a solvent with low solubility is used in film fabrication, it is difficult for the dye molecules to aggregate; or even if J aggregation is possible, the aggregates are unstable.

The fabrication method of the dye-dispersed polyvinyl alcohol (PVA) films [11,13] initially appear to be similar to ours in that spin coating is used. However, although fast spinning promotes aggregation in both fabrication protocols, our silica films differ with respect to the isotropic properties of the J aggregates in the matrices.

In Misawa and Kobayashi’s dye-dispersed films [11,13], the dye molecules in the PVA fluid are oriented by the centrifugal force that creates a fluid-dynamic flow during fabrication, giving the films dichromatic anisotropy in the direction of centrifugal force. The dichromatic spectra of our film, which were measured by changing the angle between the polarization direction and aligned axis using a polarizer (shown in **Fig. 4(a)**), are shown in **Fig. 4(b) and (c)**. The absorption spectra from 325 to 700 nm are independent of polarizer angle.
Dye sol-solution and by spin casting at 2000 rpm, was measured for the present films. The nonlinear optical and Kobayashi’s films. It appears to differ fundamentally from that in Misawaism of silica film formation from solutions to films sufficient to permit exciton delocalization. Our mechan- aggregates would be aligned by the sol crystals is below the critical size of during the evaporation of EtOH. The size of J aggregate crystals is below the critical size over which the J aggregates would be aligned by the solvent flow introduced by the centrifugal force, but the size is still sufficient to permit exciton delocalization. Our mechan- ism of silica film formation from solutions to films appears to differ fundamentally from that in Misawa and Kobayashi’s films.

Fig. 4. (a) The polarization direction and the angle axis; (b) the dependence of absorption spectra on polarizer angle; (c) the absorbance at 577 nm depending on polarizer angle.

making the film isotropic. The J aggregates embedded in the silica film appear to have formed very fine crystals during the evaporation of EtOH. The size of J aggregate crystals is below the critical size over which the J aggregates would be aligned by the solvent flow introduced by the centrifugal force, but the size is still sufficient to permit exciton delocalization. Our mechanism of silica film formation from solutions to films appears to differ fundamentally from that in Misawa and Kobayashi’s films.

Preliminary data on nonlinearity optics have been measured for the present films. The nonlinear optical properties of the film fabricated using 14 wt.% cyanine dye sol-solution and by spin casting at 2000 rpm, was measured by Z-scanning. Fig. 5 shows our experimental setup for Z-scanning. A fiber laser (775 nm, 36 MHz) was regeneratively amplified to 0.8 mJ and its signal translated into 180 fs pulses at a repetition rate of 1 kHz at arbitrary wavelengths by means of an optical-parametric amplifier. This beam was split into two components, the first acting as probe and the second acting as reference. The transmittance ratio $T(z)$ was recorded as a function of the sample position $z$. The aperture condition was adjusted for measuring nonlinear refractive index and nonlinear absorption coefficient, respectively. The measurements were performed at 77 K under vacuum (< $10^{-5}$ torr).

We used the following definition of $\chi^{(3)}$ commonly adopted for THG measurements,

$$n + ik = n_0 + nk_0 + \left( \frac{n_2}{2} \right) |E|^2$$

where $n$ and $k$ are the real part and imaginary part of the complex refractive index, $n_0$ is the index of the reference material, $k_0$ is the linear absorption coefficient, and $\gamma$ and $\beta$ are the nonlinear refraction and absorption coefficient, respectively. The $Z$-scan signals were analyzed using the transmission ratio in the following equations [16–18].

$$T_{\text{closed}}(z) = 1 + \frac{4\Delta \Phi_{0}^{Re}(z/z_0) - \Delta \Phi_{0}^{Im}(z/z_0) + 3}{[(z/z_0)^2 + 9][(z/z_0)^2 + 1]^{3/2}}$$

$$T_{\text{open}}(z) = 1 - \frac{\Delta \Phi_{0}^{Im}}{2\sqrt{(2(z/z_0)^2 + 1)}}$$

Here, $\Delta \Phi_{0}^{Re} = (2\pi/\lambda) L_{\text{eff}} I_0 L_0$ and $\Delta \Phi_{0}^{Im} = \beta L_0 I_0 L_{\text{eff}} L_{\text{eff}} = (1 - e^{-\gamma L})/\gamma L$, $L$ is the sample thickness. Eqs. (3) and (4) describe the transmittance ratios at the closed and open aperture conditions, respectively. So, $\Delta \Phi_{0}^{Re}$ and $\Delta \Phi_{0}^{Im}$ can be calculated from $T_{\text{open}}(z)$ by Eq. (4); $\Delta \Phi_{0}^{Re}$ can then be obtained from $T_{\text{closed}}(z)$ by Eq. (3) and $\Delta \Phi_{0}^{Im}$. The $\chi^{(3)}$ values were determined by the $\chi^{(3)}$ of fused silica. We used a fused silica plate as a standard material whose $\chi^{(3)}$ value was evaluated as $1.3 \times 10^{-14}$ esu. The $\chi^{(3)}$ of the film doped with J aggregates was defined as

$$\chi_{s}^{(3)} = \chi_{Re,s}^{(3)} + i \chi_{Im,s}^{(3)}$$

$$= \left( \frac{\Delta \Phi_{0}^{Re}}{\Delta \Phi_{0}^{Im}} \right) \left( \frac{L_{\text{eff}} I_0}{L_0} \right) \left( \frac{n_2}{n_0} \right)$$

$$\times \left( \frac{I_{0,s}}{I_{0,s}} \right)$$

Fig. 5. The experimental setup for Z-scan measurement.
$\chi^{(3)}_{\text{Re}}$ and $\chi^{(3)}_{\text{Im}}$ are the real part and imaginary part of $\chi^{(3)}$, respectively. $\Delta \phi^{\text{Re}}_0$ and $\Delta \phi^{\text{Im}}_0$ are the phase shifts of the beam through the sample, as derived from the Z-scan data. $L_{\text{eff}}$ is the effective thickness of the sample. $n_0$ is the linear refractive index. $I_0$ is the intensity of the incident beam. Subscript s and r stand for the sample and the reference (standard material), respectively.

The Z-scans were measured through closed and open aperture at four wavelengths: the on-resonant wavelength of 577 nm and the off-resonant wavelengths of 566, 581 and 589 nm. Fig. 6 shows the relationship between the transmittance ratio $T(\tau)$ and $Z$ at the on-resonant wavelength of 577 nm, measured through an open aperture. The solid line is the result calculated using a film thickness of 169 nm and refractive index of 1.7. The thickness and refractive index were obtained by ellipsometry.

Fig. 7 shows the wavelength dependence of the absorbance and third order susceptibility $\chi^{(3)}_{\text{Im}}$. It indicates that the film possesses a large $|\chi^{(3)}_{\text{Im}}|$ around the on-resonant wavelength ($5 \times 10^{-7}$ esu at 577 nm). It should be noted that this value is not the net value of $|\chi^{(3)}_{\text{Im}}|$. Assuming that the dye molecules migrate into the pores formed in the silica film and form J aggregates, the volume partition of the molecules is 14% in the silica film. So, the net susceptibility of $4 \times 10^{-6}$ esu is evaluated from the volume partition. On the other hand, $|\chi^{(3)}_{\text{Re}}|$ is less than $3 \times 10^{-8}$ esu at their wavelengths; the film mainly shows nonlinearity of absorption.

Although it has been predicted that J aggregates enhance third-order susceptibility, only the largest gross value of $\sim 10^{-10}$ esu has been reported [19]. For example, degenerate four-wave mixing (DFWM) and pump-probe spectroscopy have demonstrated that the $\chi^{(3)}$ of the J-aggregate, formed by 1,1'-diethyl-2,2'-cyanine chloride (PIC-Cl) molecules in an aqueous solution system, is about $1.2 \times 10^{-11}$ esu.

The same measurement system as that used by Furuki et al. was employed for pump-probe measurement. Femtosecond optical pulses of signal and idler beams were generated from an optical parametric amplifier system using a 1 kHz Ti:sapphire regenerative amplifier. The second harmonics of the beams (577 nm) and white-light continuum generated from a sapphire plate by focusing the idler beam were used as pump and probe pulses. The cross-correlation width of each pulse was about 180 fs in the measured wavelength range. Transient absorption spectra were measured using a pair of spectroscopic diode array detectors with one measuring the probe pulses transmitted through the sample and the other measuring the divided reference probe pulses. So as not to cause bleaching by only the probe pulse under illumination, the intensity of the probe pulses was attenuated to about 2.5 $\mu$J cm$^{-2}$ per pulse on the sample. To subtract the optical noise generated by self-diffraction and fluorescence caused by the pump pulses, the spectral signal observed under illumination of only the pump pulses was used as the background level. The Fig. 8 shows a typical dispersion adsorption change spectra with a decrease at a longer wavelength spectra and an increase at a shorter wavelength. These transient absorption spectra indicate a fast response of several hundred fs, similar to that of observed in other research groups' J aggregates [20–22]. The negative absorption change results from transition from the ground state to the 1-exciton state, and the positive absorption change results from transition from the 1-exciton state to the higher exciton state [20].

The delay spectra of bleached absorption change at 575.00 nm and induced absorption change at 565.92 nm were investigated and are shown in Fig. 9. There are two
components for the decay time constant for excited states of approximately 500 fs and 15 ps as seen in other reported J aggregates. In this case, with a pump energy of 2.5 µJ cm⁻², both bleached absorption change at 575.00 nm and induced absorption change at 565.92 nm showed the almost same fast and slow decay time constant. The two time constants result from the stimulated (fast) and spontaneous (slow) emissions from the 1-exciton state to the ground state.

As a result of using sol–gel processing to dope the silica film with a high density of dye molecules, our film shows a gross $|\chi_3^{(3)}|$ of approximately $10^{-7}$ esu, sufficient for direct use in practical devices. The film thus appears to have practical potential.

A sign inversion of $\chi_3^{(3)}$ is observed around the J band. The sign is negative on the longer wavelength side and positive on the shorter wavelength side in the J band, indicating the transition from bleached absorption to induced absorption around the J band. This sign inversion of $\chi_3^{(3)}$ was also observed in the solution system of J aggregates [19]. Although the material morphology of the sample is not filmlike, these inversions would essentially appear to be due to an analogous mechanism which can be explained by the two-exciton model. It consists of a three-level system: a ground state, a one-exciton state and a two-exciton state. The first exciton is formed by transition from the ground state to the one-exciton state and causes bleached absorption. Next, the second exciton is formed by transition from the one-exciton to the two-exciton state, which gives rise to induced absorption. Owing to repulsion between excitons, second excitation formation would require a higher energy than first excitation formation.

On the other hand, at off-resonant wavelengths, the film possesses $|\chi_3^{(3)}|$ of $10^{-8}$ esu. Thus, the $\chi_3^{(3)}$ is enhanced only close to the on-resonant wavelength. A similar wavelength dependence was also observed in the solution system [19]. In short, nonlinearity of J aggregates appears only around the J band.

Preliminary experiments using a pump-probe showed the film to have a response time $\tau$ of 0.5 ps under 575 nm excitation at room temperature. Kato et al. obtained a $\tau$ value of 0.3 ps for the PIC-Br solution system at 77 K [23]. This would be expected, since effective aggregated size $N$ is affected by the matrices supporting the dye molecules and the counter anions paired with the chromophores, which would consequently affect third nonlinear susceptibility $|\chi_3^{(3)}|$. For J aggregation, the effect of these factors would have to call for further consideration.

4. Conclusion

A thin silica film doped with the condensed cyanine dye J aggregates was synthesized for the first time using a brief and simple sol–gel method. A high value of third order optical nonlinearity susceptibility ($\chi_3^{(3)} = 10^{-7}$ esu) at the resonant wavelength (∼577 nm) of the J aggregates was observed. The stability of these films as demonstrated in our experiments is likely to make them useful as materials for nonlinear optical devices. However, improvements are needed concerning optical instability caused by dye decomposition reactions with atmospheric oxygen. An improved synthesis process is under development, and the nonlinear properties of the silica film doped with J aggregates synthesized using an improved method are being investigated at room temperature and pressure.

References