

Aqueous dispersion of J-aggregates and J-aggregate doped bulk-gels prepared by the dispersion

Keiji Yamamoto, Noritaka Kato* and Yoshiaki Uesu,

Department of Physics, Waseda University, Tokyo 169-8555, Japan

Fax: 81-3-5286-3446, *e-mail: n.k@waseda.jp

We have prepared silica bulk-gels doped with merocyanine J-aggregates by a sol-gel method. The obtained bulk-gels had high transparency and the J-aggregates were doped uniformly. The merocyanine concentration of 69 nmol/cm^3 was achieved. The preparation conditions of J-aggregate doped bulk-gels and their visible absorption properties were reported.

Key words: J-aggregate, bulk-gels, dispersion, sol-gel method

1. INTRODUCTION

J-aggregates are assemblies of organic dye molecules with ordered structures. They show a sharp, intense and red-shifted visible absorption band with respect to that of monomeric dye molecules. They have a large nonlinear optical property [1] and are used as spectral sensitizers of silver halides in photography [2].

For applications in optical technologies, various optical properties of the J-aggregates have been studied [3-12] and, to have better mechanical, chemical and physical stabilities, the J-aggregate doped silica films were prepared using sol-gel methods [1,13,14]. The present work has been devoted to dope the J-aggregates formed by amphiphilic merocyanine dye (MD) molecules (Fig. 1) in a silica matrix.

Besides the various investigations on the MD J-aggregate films, such as Langmuir-Blodgett [15,16], vapor deposition [17] and cast films [18], we made aqueous liposome dispersions of MD J-aggregates [19]. The MD J-aggregates were dispersed together with liposome-forming lipids in aqueous media. Our aim is to dope the MD J-aggregates in a silica matrix using their aqueous dispersion. The advantage of the use of the J-aggregate dispersion is that we could easily control the doping concentration of the J-aggregates without concerning the conditions for the J-aggregate formation during the sample preparation. So far, monomeric dye molecules were mixed in the sol solution and they assembled into the J-aggregates during the gelation and the drying process of the sol solution [1,14]. In these cases, the J-aggregate formation depended on a rotating speed in a spin-coating method [1] and the drying conditions [14]. Therefore, if the J-aggregates themselves were dispersed in the sol solution, wider conditions for doping the J-aggregates in the silica matrixes could be realized.

2. EXPERIMENTAL

The MD molecules were purchased from Hayashibara Biochemical Laboratory, Inc., and the phospholipids (1,2-dimyristoyl-*sn*-glycero-3-phosphocholine, DMPC) were purchased from NOF Corporation. Methyl-triethoxysilane (MTES, Fig. 2(a)) and tetraethyl-ortosilicate (TEOS, Fig. 2(b)) were obtained from Acros Organics and Wako Pure Chemical Industries,

Ltd., respectively. Pure water used was prepared in a Milli-Q system.

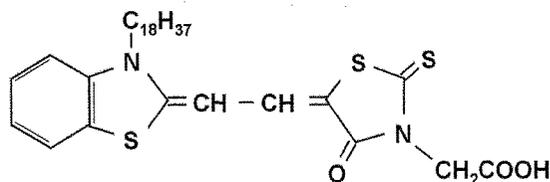


Fig. 1 Molecular structure of merocyanine dye

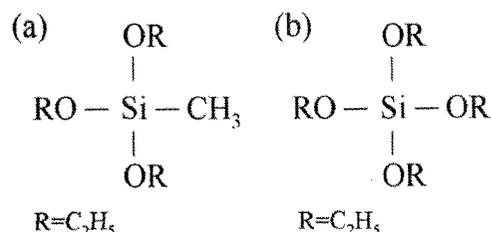


Fig. 2 Molecular structures of (a) MTES and (b) TEOS.

A full description for the preparation of the J-aggregate dispersion was found in Ref. [19]. In brief, $0.16 \mu\text{mol}$ of MD and $0.32 \mu\text{mol}$ of DMPC were dispersed in 4 mL of 1 mM CdCl_2 aqueous solution. NaHCO_3 was added to keep the pH value around 6.3.

For the MD J-aggregate doping, the conditions for entrapping liposomes in the silica matrices [20-23] were referred. A mixture of TEOS (9.38 g) and MTES (1.04 g) was added in a solution consisting of 9 g of pure water, 0.76 mL of 0.04 N aqueous HCl and 5.06 g of ethanol. The resultant mixed solution separated in two phases. This solution was stirred for 2 hours by a magnetic stirrer at 1200 rpm to obtain a one phase clear solution. During this stirring period, TEOS and MTES were hydrolyzed and polycondensation reaction occurred, resulting in the sol solution. To the sol solution, a mixture of pure water (25 g) and 0.01 N aqueous ammonia (3.75 mL) was added drop by drop to adjust the pH from acidic to neutral, followed by stirring

for 2 hours. 0.5 g of the J-aggregate dispersion was then added to 3.5 g of the sol solution and 3 minute stirring was followed. The sol solution added with the J-aggregates was poured into an acryl cylinder of 31 mm diameter and was incubated in dark for gelation and drying. All procedures were carried out at a room temperature.

Absorption spectra of the samples were measured by UV-visible recording photo-spectrometer (UV-2100, Shimadzu).

3. RESULTS AND DISCUSSION

The above condition was found out to obtain the uniformly doped, transparent, crack free, and mechanically hard silica bulk-gels without any precipitation and dissociation of the MD J-aggregates.

The mixture ratio of water and ethanol affected the hydrolyzation speed of the alkoxides and the J-aggregate dispersion. An increase of the ratio of ethanol than the above condition resulted in an increase of the hydrolyzation speed. However, the precipitation and dissociation of J-aggregates in the sol solution occurred.

The pH of the sol solution infected the transparency of the gel and the dispersity of the J-aggregates. The acid catalyst (HCl) was used to obtain a transparent sol solution. However, the acidic condition resulted in the precipitation of the J-aggregates and cracks in the gel. Therefore, before adding the J-aggregate dispersion, the aqueous ammonia was added to make the solution neutral. When NaOH was used instead of ammonia, the obtained bulk-gels had a poor mechanical stability and were easily broken into small pieces.

The blend ratio of MTES and TEOS was also an important parameter to have the uniform and transparent J-aggregate doped silica bulk-gels. Because MTES has one methyl group that is not responsible for the hydrolysis reaction (Fig. 2(a)), the addition of MTES to TEOS leads to a less dense SiO₂ network and gives a slight plasticity to the silica. Due to this effect, the resultant silica gel was not easily broken in comparison with the silica gel obtained without MTES. However, as the amount of MTES increased, the gelation speed of the sol solution decreased and the J-aggregates precipitated in the gel. Therefore, we adjusted the mixture ratio of TEOS and MTES at 9.38 g and 1.04 g, respectively, to let the sol solution lose its liquidity within 2 days.

The increase in the adding amount of the aqueous dispersion of the J-aggregates in the sol solution promoted the generation of cracks in bulk-gels during the drying process. This tendency might be caused not by the J-aggregates but by the increase of water content in the sol solution [24]. Above the weight ratio between the J-aggregate dispersion and the sol solution of 1 : 3, the crack generation became significant. Therefore, we prepared at the ratio of 1 : 7 in the preset work.

The drying process to form the bulk-gel was performed in the acryl cylinder. When the sol solution was lost its liquidity, a wet gel was formed. The wet gel was so soft and fragile that it could not be taken out from the cylinder without breaking into pieces. The shrinkage of the wet gel during the drying process detached the gel from the cylinder wall and increased the mechanical strength of the gel, resulting in the formation of the bulk-gel. These shrinkage effects that

were achieved by drying at least 3 weeks made us easy to take out the bulk-gel from the cylinder.

The photographs of the obtained J-aggregate doped silica bulk-gel, which was taken out from the cylinder, are shown in Fig. 3. Although there are two cracks, it is transparent and the uniform doping of the J-aggregates was achieved. Fig. 3(a) shows the bulk-gel after 4 week drying. The bulk-gel had a diameter of 27 mm and a thickness of 1.6 mm. Fig. 3(b) indicates the same sample after 5 week drying. The bulk-gel shrank in a diameter of 17 mm and a thickness of 1.4 mm. The volume of (a) was reduced to ca. 1/3 in (b).

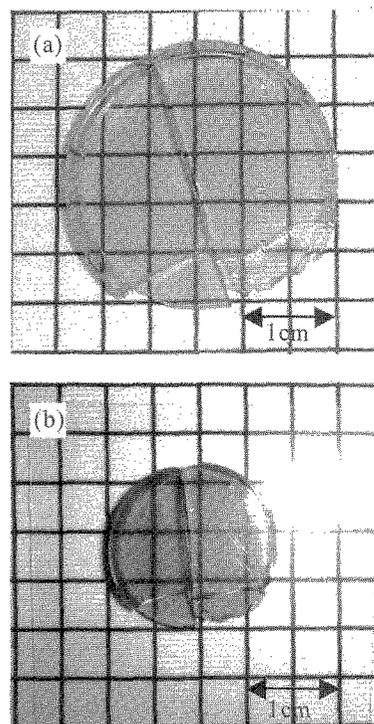


Fig. 3 The photographs of the J-aggregate doped silica bulk-gel. The bulk-gel dried for (a) 4 weeks and (b) 5 weeks after the preparation of the sol solution. The mesh lines can be seen clearly through the gel, indicating that the obtained gel was transparent and uniform.

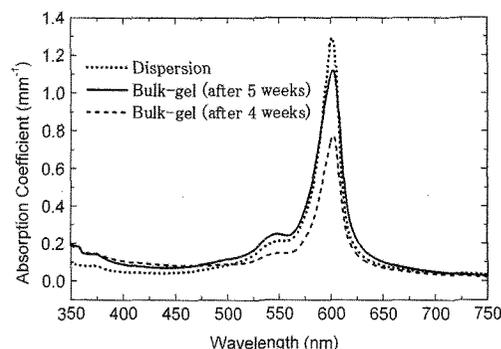


Fig. 4 The visible absorption spectra of the samples. Dash and solid lines indicate spectra of the bulk-gel shown in Fig. 3 (a) and (b), respectively. Dotted line indicates the spectrum of the aqueous J-aggregate dispersion before doping.

Table 1 The absorption properties and the dye concentrations of the bulk-gel and the J-aggregate dispersion.

	Aqueous dispersion	Bulk-gel	
		After 4 weeks	After 5 weeks
Peak wavelength (nm)	601.5	602	602
FWHM (nm)	23	26	30
Dye concentration (nmol/cm ³)	80	51.2	69

Fig. 4 shows the visible absorption spectra of the obtained J-aggregate doped silica bulk-gel and the J-aggregate dispersion. According to the shrinkage of the sample observed in Fig. 3, the absorption coefficient of the 5 week passed bulk-gel is estimated to be 2.88 times larger than that of the 4 week passed sample. However, the actual increase was only 1.35 times as shown in Fig. 4 (Dash and solid lines), indicating the discoloration of the MD molecules during the drying process. On the other hand, as indicated in Table 1, the absorption peak wavelengths and the full widths at half maximum (FWHM) of the peaks in Fig. 4 are almost the same, indicating that apparently there was no dissociation of the J-aggregates during the drying process. These results imply that there are two possibilities on the discoloration mechanism: (1) the J-aggregates are directly decomposed, (2) the J-aggregates are gradually dissociated and the resultant monomers are decomposed too rapidly to be detected in the spectra. The dye concentrations in the bulk-gel dried for 4 and 5 weeks were calculated by the absorption coefficients at the peaks, and were 51.2 and 69 nmol/cm³, respectively. The dye concentration of the 5 week passed bulk-gel was reached to 85% of that of the aqueous dispersion.

4. SUMMARY

We doped the MD J-aggregates in a silica matrix using the sol-gel method. The obtained silica bulk-gels were transparent and the J-aggregates were doped uniformly in the matrix. The dye concentration in one of the bulk-gels was 69 nmol/cm³. According to the visible absorption spectra of the J-aggregates doped bulk-gel, the monomer absorption band was not observed for 5 weeks.

5. ACKNOWLEDGEMENTS

The authors are grateful to Dr. K. Katagiri for his fruitful discussions on the sample preparation. This work was supported by the Saneyoshi Scholarship Foundation and Grant-in-Aids for Young Scientists (B) 17760015, 2005 and The 21st Century COE Program (Physics of Self-Organization Systems) at Waseda University from MEXT, Japan.

References

- [1] H. S. Zhou, T. Watanabe, A. Mito, K. Asai, K. Ishigure, I. Honma, *J. Sol-Gel Sci. Tech.* **19**, 803 (2000).
 [2] T. Tani, *J. Disp. Scie. Technol.* **25**, 375 (2004).

- [3] M. Furuki, M. Tian, Y. Sato, L. S. Pu, S. Tatsuura, O. Wada, *Appl. Phys. Lett.* **77**, 472 (2000).
 [4] A. V. Vannikov, A. D. Grishina, B. I. Shapiro, L. Y. Pereshivko, T. V. Krivenko, V. V. Savelyev, V. I. Berendyaev, R. W. Rychwalski, *Chem. Phys.* **287**, 261 (2003).
 [5] R. Gagel, R. Gadonas, A. Laubereau, *Chem. Phys. Lett.* **217**, 228 (1994).
 [6] K. Sayama, K. Sayama, S. Tsukagoshi, K. Hara, Y. Ohga, A. Shinpou, Y. Abe, S. Suga, H. Arakawa, *J. Phys. Chem. B.* **106**, 1363 (2002).
 [7] F. Meng, K. Chen, H. Tian, L. Zuppiroli F. Nuesch, *Appl. Phys. Lett.* **82**, 3788 (2003).
 [8] S. de Boer, K. J. Vink, D. A. Wiersma, *Chem. Phys. Lett.* **137**, 99 (1987).
 [9] M. S. Bradley, J. R. Tischler, V. Bulović, *Adv. Mater.* **17**, 1881 (2005).
 [10] D. G. Lidzey, A. M. Fox, M. D. Rahn, M. S. Skolnick, V. M. Agranovich, S. Walker, *Phys. Rev. B.* **65**, 195312 (2002).
 [11] N. Tamaoki, E. V. Keuren, H. Matsuda, K. Hasegawa, T. Yamaoka, *Appl. Phys. Lett.* **69**, 1188 (1996).
 [12] K. Misawa, H. Ono, K. Minoshima, K. Kobayashi, *Appl. Phys. Lett.* **63**, 577 (1993).
 [13] J. Tang, Y. Wang, D. Yu, Z. Zhou, C. Wang, B. Yang, *Mater. Lett.* **50**, 371 (2001).
 [14] U. de Rossi, S. Daehne, R. Reisfeld, *Chem. Phys. Lett.* **251**, 259 (1996).
 [15] M. Sugi, T. Fukui, S. Iizima, K. Iriyama, *Mol. Cryst. Liq. Cryst.* **62**, 165 (1980).
 [16] K. Iriyama, M. Yoshimura, Y. Ozaki, T. Ishii, S. Yasui, *Thin Solid Films* **132**, 229 (1985).
 [17] Y. Ueda, K. Nitta, *Jpn. J. Appl. Phys.* **40**, 6951 (2001).
 [18] K. Iriyama, F. Mizutani, M. Yoshiura, *Chem. Lett.*, 1399 (1980).
 [19] N. Kato, J. Prime, K. Katagiri, F. Caruso, *Langmuir* **20**, 5718 (2004).
 [20] I. Gill, *Chem. Mater.* **13**, 3404 (2001).
 [21] W. Jin, J. D. Brennan, *Anal. Chim. Acta* **461**, 1 (2002).
 [22] S. A. Yamanaka, D. H. Charych, D. A. Loy, D. Y. Sasaki, *Langmuir* **13**, 5049 (1997).
 [23] T. Huyen, K. P. McNamara, Z. Rosenzweig, *Anal. Chim. Acta* **400**, 45 (1999).
 [24] T. Adachi, S. Sakka, *J. Non-cryst. Solids* **99**, 118 (1988).

(Received December 11, 2005; Accepted January 30, 2006)