Available online at www.sciencedirect.com

ScienceDirect

Thin Solid Films 516 (2008) 2363 – 2370

www.elsevier.com/locate/tsf

Self-organized dye particles: Role of dewetting process in molecular ordering

Akihiro Tomioka [a,b,*], Shinji Kinoshita [a], Atsushi Fujimoto [a]

[a] Graduate School of Engineering, Osaka Electro-Communication University, 18-8 Hatucho, Neyagawa, Osaka 572-8530, Japan
[b] Academic Frontier Promotion Center, Osaka Electro-Communication University, 18-8 Hatucho, Neyagawa, Osaka 572-8530, Japan

Abstract

Self-organized rhodamine 6G particles prepared by wetting/dewetting process of an ethanol solution on a hydrophilic glass surface exhibited fluorescence without quenching, showing a sharp linewidth of 2 nm with a large redshift, which indicates an existence of dye aggregates, similar to J aggregates, inside the particle. Polarized evanescent field excitation showed that the dye molecule's transition moment along the π-conjugation was oriented unidirectionally within particles and parallel to the substrate surface. This deduced dye orientation showed correlation between adjacent, however separated, particles, and pointed roughly 45° off the dewetting direction. In contrast, another π-conjugated NK1420 dye, J aggregates of which grow easily from an oversaturated solution, yielded particles with constituent dyes oriented along the dewetting direction preferably, still indicating the effect of self-organization, however based on a different mechanism.

Keywords: Self assembled; Dewetting process; Pi conjugated dye; J aggregate; Evanescent field; Molecular orientation

1. Introduction

Much attention has been paid to organic materials in recent years for their potential applications in electronics and photonics [1]. The main advantage of organic materials is that they can be fabricated onto almost any type of substrate (including flexible ones) by inexpensive techniques, like spin coating and inkjet printing, in contrast to the more elaborate and sophisticated processing used with inorganic materials. For nanostructure fabrication, dewetting process of a solution specimen on a solid substrate is favorable for fabricating self-organized nanostructure because it provides a very rapid processing over huge surface area in an ambient condition.

For photonic applications π-conjugated dyes are major concerns due to its superior optical responses: high oscillator strength of the π–π* transition of the conjugated π orbital and its wide tunability in wavelength via molecular design. Some dye species, e.g. those providing J aggregates [2], of π-conjugated dyes show high quantum efficiency of photoluminescence, although others get completely quenched when placed in a solid state. Investigation of how dye aggregation affects these optical behaviors is, therefore, of importance not only for application purpose but also from a fundamental point of views: the knowledge of how the molecular interaction leads to the optical behavior of the aggregates would produce a novel chemical design of dye aggregates with efficient optical properties.

Here we present a fabrication of self-organized aggregates of two types of π-conjugated dyes, one is known to produce a two-dimensional J aggregate [3,4] and the other is thought to get quenched in a solid generally. Mode of aggregation and the distribution of dye orientation are investigated, leading to discussions on possible dye aggregation mechanism.

2. Materials and methods

We adopted the π-conjugated organic dyes rhodamine 6G (Rh6G) and NK1420 (5,6-dichloro-2-[3-(5,6-dichloro-1,3 diethyl-2(3H)-benzimidazolylidene)-1-propenyl]-1,3-diethyl-benzimidazolium iodide) for the present study because both have a static positive charge so that they are expected to interact

---

* Corresponding author. Graduate School of Engineering, Osaka Electro-Communication University, 18-8 Hatucho, Neyagawa, Osaka 572-8530, Japan. Tel.: +81 72 824 1131; fax: +81 72 824 0014.
E-mail address: tomioka@isc.osakac.ac.jp (A. Tomioka).

0040-6090/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2007.04.097

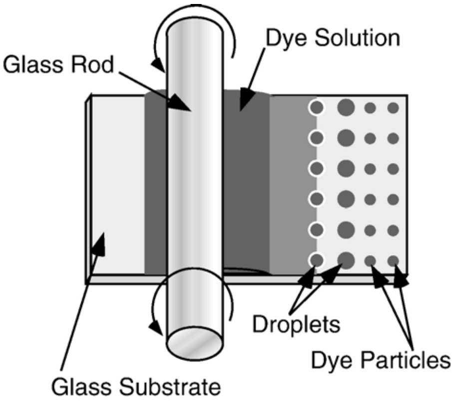

Fig. 1. Schematic diagram showing the wetting/dewetting procedure to prepare self-organized dye particles. To control the thickness of the ethanol solution of the Rh6G dye, a glass rod was pressed against a glass substrate surface and rolled over it. At a critical solution film thickness during the evaporation of ethanol, the solution film becomes separated into droplets and then dye particles are precipitated. The critical solution film thickness was controlled by the hydrophilicity of the substrate surface, which is accomplished by a prior ozone processing. Images in the following figures will be placed so that the movement of the glass rod is from right to left.

strongly with a hydrophilic glass surface with an exposed O^- group [5]. The hydrophilic glass surface also promoted a wetting/dewetting process [6] of polar organic solvent upon it, which is the primary motive force realizing the self-organizing formation of submicrometer-sized particle arrays of the dye [7]. When a glass rod slid over a 100 μl ethanol solution of typically 30 μg/ml Rh6G (Fig. 1), a very thin layer of Rh6G solution was formed. Thickness of the solution layer became thinner while the solvent ethanol evaporated naturally from it. At certain thickness the solution layer became separated into droplets, and then dye particles were formed as precipitates after the solvent further evaporated. Since the particle size would be determined by the number of dye molecules which is proportional to the droplet size left on the surface, and therefore by the wetting/dewetting process of the organic solvent, the size was controlled by the degree of the surface hydrophilicity and by changing the retraction velocity of the solvent boundary when it evaporated [7]. The same dewetting procedure was used to prepare NK1420 dye particles, but the dye was dissolved in methanol for solubility.

3. Results and discussion

3.1. Far-field fluorescence of Rh6G particles excited by s- and p-polarized evanescent field

Under an epifluorescence microscope, all the self-organized particles showed fluorescence as shown in Fig. 2(a), which is a unique characteristic of the present specimen, because Rh6G fluorescence was generally regarded to be quenched in a solid state. How the dyes are stacked in the particle should be different from that in conventional Rh6G precipitates. Under photoexcitation by an incoherent light, every particle shows a sharp fluorescence spectrum having a full linewidth of 2 nm with a large redshift ([8], Fig. 2(b)), which indicates an existence of dye aggregates, similar to J aggregates, inside the particle.

To elucidate the mode of dye stacking we investigated the dye orientation inside the particle by observing the far-field fluorescence when the particles were photoexcited by linearly polarized evanescent field [Fig. 2(e)]. Using a polarized green light ($510\ \text{nm} < \lambda < 560\ \text{nm}$) excitation, the π–π^* transition moment along the π-conjugation was effectively probed. In the following, the direction of this transition moment is referred to as the direction of a molecule. For evanescent field observation, the incident laser ($\lambda = 532$ nm) polarization was selected by a film polarizer as p- or s-polarized for Fig. 2(c) or (d), respectively, that had the same intensity after the laser was guided through an enough length (>10 m) of multimode optical fiber and was accurately collimated with an aspheric lens. Let us point out three observations: (A) some of the particles showed strong fluorescence [enclosed in solid ellipses in Fig. 2(c)] when excited by a p-polarized evanescent field, indicating that dye molecules within these particles were oriented in the zx-plane. (The incident laser spot was larger than the field of view and was almost uniform within this picture.) (B) Fig. 2(d) shows a different distribution of fluorescence intensity when the particles are excited by an s-polarized evanescent field. Particles enclosed in solid ellipses show weak fluorescence. In contrast, those in dotted ellipses show strong fluorescence, indicating that dye molecules within them should be oriented in the y-direction. (C) On the other hand, we detected no difference in Fig. 2(a), even if we set the far-field excitation to be polarized in the x- or y-direction.

Observation (C) suggests that the majority of dye molecules within a particle are distributed randomly within the xy-plane and observations (A) and (B) indicate that only dyes near the surface have a unidirectional orientation within each particle [Fig. 2(f)]. The evanescent field was expected to extend out into the air about 100 nm from the surface at a wavelength of 532 nm, which justifies our prediction that only surface dyes would be observed in the evanescent field excitation. If the transition moment of dye molecules has a z-component, it should appear as a bright particle in Fig. 2(c) but disappear in Fig. 2(d). The fact that no candidate for this type of particle can be found in the figures suggests that surface dyes in a particle are oriented unidirectionally and dominantly within the xy-plane. The fluorescence in Fig. 2(c) was, therefore, due to only the x-component of the evanescent field that was expected to have a rotating field direction [9,10] within the zx-plane when excited by a p-polarized light.

The unidirectional orientation of only surface dyes may be ascribed to the strong electrostatic interaction between the dye molecule's positive charge [Fig. 2(f)] and the glass surface's negative charge [Fig. 2(g)]. How this electric attractive force and the capillary force lead to the self-organization of dye aggregates in a particle is still an open question.

In Fig. 2(c) and (d), the molecules in adjacent particles seem to be oriented in a similar direction because they have similar intensities. This observation suggests that the dewetting process contributed to the alignment of the molecular direction among adjacent particles, which further proves that the dye particles were formed by a self-organizing mechanism. Then what is the actual mechanism of dye orientation correlation in the course of dye aggregates formation from solution droplets?