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A wetting/dewetting process was utilized to prepare a self-organized formation of organic dye particles of micrometer and submicrometer size in one- or two-dimensional registration. The near-field scanning optical microcopy (NSOM) study successfully identified near-field-excited near-field fluorescence from single particles. The majority of small particles with diameters around 2 μm or less, however, did not show fluorescence under near-field observation. In contrast, far-field fluorescence, when excited by a polarized evanescent field, was observed, with the intensity depending on the excitation polarization. This indicates that molecule transition moment within dye particles was oriented parallel to the substrate surface. These observations suggest that the near-field at the probe tip was polarized parallel to the probe axis. Another observation, that molecules were oriented in a similar direction among adjacent particles, suggests that the dewetting process contributed to the alignment of the molecular direction among adjacent particles, which further proves that the present specimen was formed by a self-organizing mechanism.

Keywords: π conjugated dye; dewetting process; evanescent field; molecular orientation; near field; self assembled

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INTRODUCTION

We previously reported that some J-aggregates showed a very narrow absorption/fluorescence spectrum with a large red shift [1] and we explained this phenomenon on the basis of theoretical model of two-dimensional excitons whose wavefunctions spread over more than 100 dye molecules, whereas fluorescence was emitted dominantly from only few localized excitons formed due to spatial disorder at the excitation band bottom [2]. We are now interested in the exciton behavior when the aggregate is prepared under electrostatic interaction with a hydrophilic surface. Here we report such a fabrication by self-organizing procedures and a near-field and evanescent-field optical study of π-conjugated organic dye particles to discuss the molecular orientation within these dye particles.

MATERIALS AND METHODS

We adopted the π-conjugated organic dye rhodamine 6G (Rh6G) for the present study because it is stable and the extent of photobleaching is small when it is irradiated by strong laser light. The Rh6G molecule has a static positive charge so that it is expected to interact strongly with a hydrophilic glass surface with an exposed O group. The hydrophilic glass surface also promoted a wetting/dewetting process [3] of organic solvent upon it, which is the primary motive force realizing the self-organizing formation of submicrometer-sized particle arrays of the dye [4]. When a glass rod slid over a 100 μl ethanol solution [Fig. 1(a)], a very thin film of ethanol solution was formed. Particles were formed as precipitates when the solvent ethanol evaporated naturally from this thin layer of dye solution. Since the particle size would be determined by the number of 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 [4].

Dichroic mirror optics was used to separate the specimen fluorescence from the excitation laser (Nd/YAG SHG). The specimen particle was optically excited with the near-field at the tip of an optical probe and the near-field component of the specimen fluorescence was collected with the same probe. Pure-silica optical fiber was used to couple the laser into the probe in order to suppress the background fluorescence from the probe fiber.

To investigate the molecular orientation within particles the specimen was excited by an evanescent field at the substrate glass surface that was produced by a *p*- or *s*-polarized Nd/YAG SHG laser in a

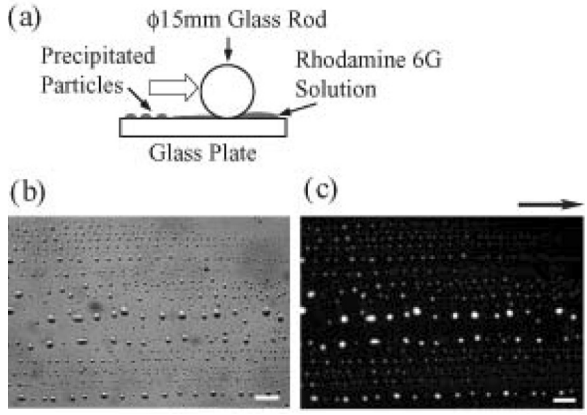

FIGURE 1 (a) Schematic view showing the wetting/dewetting procedure to control the thickness of the ethanol solution of the Rh6G dye, which is accomplished by pressing a glass rod against a substrate surface whose hydrophilicity was controlled by a preceding ozone processing, leading to a self-organized formation of dye particles. (b) and (c) Optical microscope images of a Rh6G self-assembled array, the reflection image and the fluorescence image, respectively. An arrow shows the direction of the glass rod movement in specimen preparation. Bars indicate 20 μm.

configuration of total internal reflection. The resulting far-field fluorescence was collected by an objective lens and dichroic mirror optics in a conventional fluorescence microscope. For comparison, far-field-excited far-field fluorescence was also recorded.

To measure the far-field fluorescence spectra of single particles, the specimen was positioned on a microscope stage so that the target particle was located at the center of the field of view and only the particle was photoexcited using the variable aperture of the microscope's illumination optics. Fluorescence spectra were recorded by a high-efficiency back-illuminated charge-coupled device camera cooled doubly with two Peltier elements to reduce the dark noise. We used the minimum gain of the on-chip multiplication of accumulated electrons and accumulated them for 30 s. We did not use image intensifier because it was found to produce persistent fluctuations even after long exposure.

RESULTS AND DISCUSSION

Self-assembled Arrays of Dye Particles

In the reflection image of an optical microscope [Fig. 1(b)], one can observe large particles with 2 to 5 μm diameters and small ones

with $< 1\,\mu m$ diameter. Particles with similar diameters seem to be arranged in the direction of glass rod movement (from left to right). Note that there is no clustering of particles, which is one of the best characteristics of the present procedure, enabling us to easily distinguish optical responses from separate particles. All the particles were made of Rh6G because all of them can be observed in the epifluorescence image in Figure 1(c). We need to refine the surface treatment procedure to obtain particle arrays with uniform diameters.

Near-field Fluorescence of Dye Particles

We used a pure silica (undoped) optical fiber to couple the laser and successfully reduced nonnegligible background fluorescence from the fiber down to 8%. Then each dye particle was discriminated in the near-field fluorescence image: Part of the surface topography in Figure 2(b) corresponded to intense fluorescence in Figure 2(a), whereas other regions did not correspond, indicating that there were nonfluorescing particles. The majority of the particles seemed optically inactive in Figure 2(c) when we observed a region of more than 100 submicrometer particles, although we scanned the area only once under photoexcitation to suppress the possible dye photobleaching. Our probe tip had the necessary resolution and the detector had sufficient sensitivity because we indeed detected a definite fluorescence over the background from some of the particles of submicrometer size.

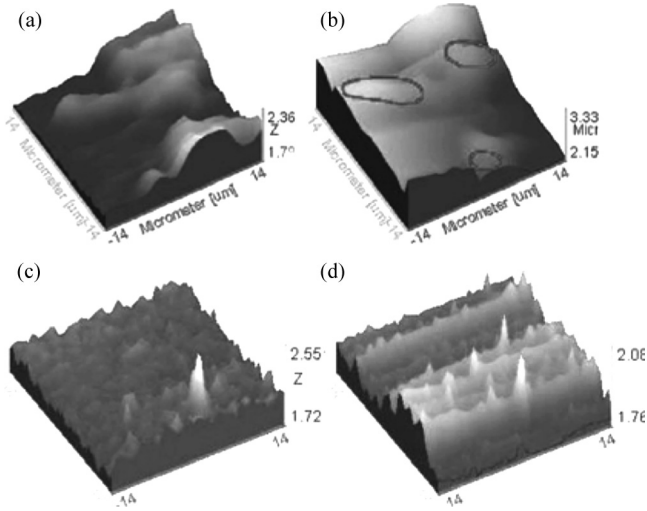

FIGURE 2 Near-field fluorescence of (a) large and (c) small particles within a Rh6G self-organized array, and (b) and (d) are the corresponding topography.

Far-field Fluorescence of Dye Particles Excited by Polarized Evanescent Field

To elucidate the origin of the missing fluorescence we then compared different excitation methods: the specimen was photoexcited by a linearly polarized (*p*- or *s*-polarized) evanescent field and far-field fluorescence was monitored (Fig. 3). Using an epifluorescence microscope, we also recorded conventional far-field-excited far-field fluorescence

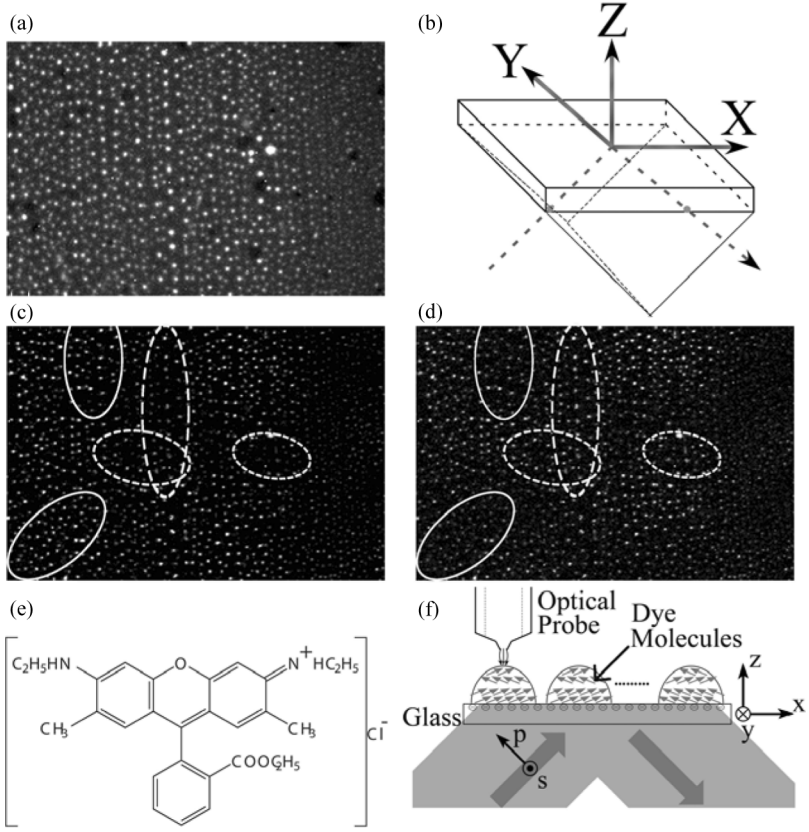

FIGURE 3 (a) Conventional epifluorescence image and (c) and (d) far-field fluorescence when excited with *p*- or *s*-polarized evanescent field, respectively, at the substrate glass surface. Corresponding regions are marked by solid and dotted ellipses. Configuration of the incident laser with respect to the substrate is depicted in (b). (e) The molecular structure of Rh6G molecule, (f) a model of alignment of dye molecules inside each particle with correlation between adjacent particles.

images as shown in Figure 3(a). Let us point out three observations: (A) Some of the particles showed strong fluorescence [enclosed in solid ellipses in Figure 3(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) Figure 3(d) shows a different distribution of fluorescence 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. The intensity contrast Ip/Is, where Ip and Is denotes the particle fluorescence under *p*- or *s*-polarized evanescent field excitation, respectively, was higher for small particles, distributing 2.6 to 5.0 for the solid ellipses region and 0.76 to 0.91 for the dotted ellipses region, which suggests that the degree of dye orientation is higher in small particles. (C) On the other hand, we detected no difference in Figure 3(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 is 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. 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 is tilted off the *xy*-plane and if this tilt angle is different among particles, particles with tilted dyes could absorb less excitation light of vertical incidence and should emit less fluorescence [Figure 3(a)], whereas for the solid ellipses region in Figure 3(c) tilted dyes could absorb *p*-polarized field and emit fluorescence fully. 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 dominantly within the *xy*-plane, or, even they are tilted off the *xy*-plane, the tilt angle may be uniform. The missing fluorescence in the near-field optical microscope (NSOM) study may then be explained if all the dyes within a particle oriented within the *xy*-plane and the near-field at the NSOM probe tip is polarized perpendicular to them. This means that the near-field of the NSOM probe is polarized parallel to the probe axis, which is in contrast to the electromagnetic field of the transverse propagating modes of the probe fiber.

In Figures 3(c) and 3(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 present specimen was formed by a self-organizing mechanism.

Far-field Fluorescence Spectroscopy of Single Particles

The unidirectional orientation of only surface dyes may be ascribed to the strong electrostatic interaction between the dye molecule's positive

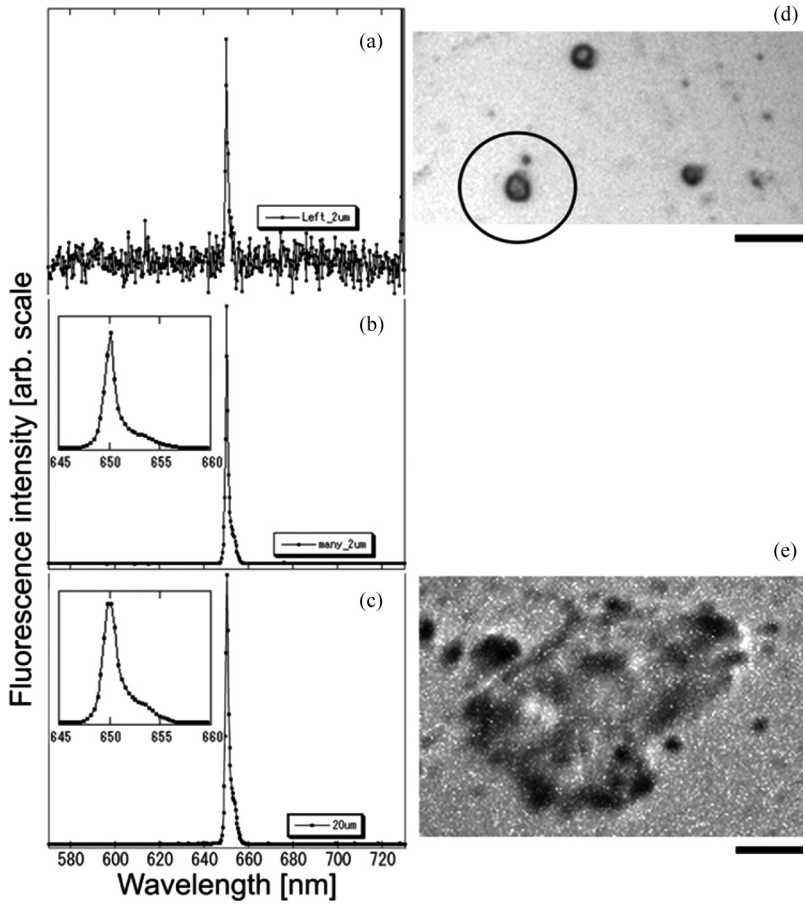

FIGURE 4 Far-field fluorescence spectra of (a) the self-organized single particle encircled in (d), and (b) more than 100 particles, and (c) the flat-sheet structure shown in (e). They are vertically scaled so that the peak height becomes similar for accurate comparison. Bars indicate 5 μm. Narrow peak width is depicted in the enlarged insets.

charge [Fig. 3(e)] and the glass surface's negative charge [Fig. 3(f)]. How this electric attractive force and the capillary force lead to the self-organization of some types of dye aggregate(s) in a particle is still an open question. To elucidate the nature of this dye aggregate, we measured the far-field fluorescence spectra of single particles. Figure 4(a) is the fluorescence spectrum of the encircled particle (2 μm diameter) in Figure 4(d), which is a reflection image magnified from part of a microscope's field of view. Two other particles in Figure 4(d) showed essentially the same sharp spectra. The spectrum was also indistinguishable (Fig. 4(b)) even if we removed the aperture and accumulated a fluorescence of more than 100 particles. Incidentally, we found a flat-sheet structure, shown in Figure 4(e), that showed the same fluorescence spectrum shown in Figure 4(c). All these structures showed a fluorescence peak at 650 nm that was 50 nm redshifted from that of a dye solution in ethanol. (The small size of the particles made it difficult to record the absorption spectrum, but it should also be redshifted similarly.) A shoulder can be observed around 653 nm that might reflect the vibrational mode of the dye molecule. The full width at the half of the fluorescence maximum was about 2 nm, as indicated in the figure insets, which is a strong indication that these structures were composed of aggregates similar to J-aggregates. Although we cannot find any report of J-aggregates made from Rh6G [5], similar aggregates should exist within the self-organized particles. They might be stable only when dye molecules attach strongly to the glass substrate due to electrostatic attraction.

CONCLUSIONS

Self-assembled arrays of submicrometer particles of organic dye were fabricated using the controlled wetting/dewetting procedure, which showed a well-dispersed distribution of particles in the one- or two-dimensional register and was favorable for single particle analyses through high-resolution optical study. We successfully detected the near-field-excited near-field fluorescence from single particles within thusly prepared specimens, whereas the majority of small particles did not show near-field fluorescence.

From the polarized evanescent-field excitation study, the transition moment of the molecule within self-assembled small particles was shown to point parallel to the substrate surface. Therefore, the fact that these particles show no fluorescence in the near-field study suggests that the near-field at the probe tip was polarized parallel to the probe axis, which shows a definite difference from the direction of the propagating transverse mode within an optical fiber. Far-field

fluorescence spectroscopy of single particles revealed that each particle was composed of some types of well-defined and essentially the same aggregates, similar to the J-aggregates, that had the same electronic band structure.

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