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Near-Field Optical Characterization of Sub-Micrometer Particle Arrays of Organic Pigment

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Sub-micrometer sized particles of organic dye, formed as precipitates on a glass surface when the organic solvent evaporated from a thin film of specimen solution at a precisely controlled evaporation rate, showed a typical one- or two-dimensional registration. We performed a near-field optical study of a single (or a few) particle(s) within these self-assembled particle arrays. Suppressing the background fluorescence that originated from the stray light in the clad region of probe fiber at the coupling point of the incident laser, we could manage to observe the near-field fluorescence from the separated particle. Further to overcome the near-field fluorescence decay in a minute or so, which was presumably due to photobleaching of surface-rich dye particles, we prepared them embedded in a transparent polymer film which is expected to protect the dye from oxygen.

Keywords: near-field; organic dye; self-assembled

INTRODUCTION

Organic dyes have many superior characteristics over inorganic ones: vast chemical species with different functional groups, covering almost

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every wavelength of absorption and fluorescence from ultra-violet to infrared; high quantum efficiency of photo-excitation; transduction capability of photon energy to chemical or mechanical energy; ease of chemical linking to other reagents with redox reactivity, biological receptors, and so on. Recently prevailing CD-R media prove that organic dyes can be active and stable even in the dried state if we isolate them from oxygen. In this paper we report the fabrication of self-assembled organic dye particle arrays utilizing the wetting/dewetting process of a glass substrate to the volatile solution. We report also a near-field optical study of separate particles of the thus formed specimens.

MATERIALS AND METHODS

Preparation of Micrometer or Sub-Micrometer Particle of Organic Dye

Sub-micrometer sized particles of organic dye rhodamine 6 G were prepared from thin layer of ethanol solution on a glass surface. This dye was selected because it is stable and extent of photobleaching is small when irradiated by strong laser light. Particles were formed as precipitates when the solvent ethanol evaporated. Since the particle size was expected to be determined by the wetting/dewetting process of the substrate surface to the organic solvent, we controlled the size by changing the degree of hydrophilicity of the surface and by changing the retraction velocity of the solvent boundary when it evaporated [1].

This boundary retraction velocity was controlled by the movement of a glass rod (circular cross section with 15 mm diameter) that was pressed against a 100 μl ethanol solution (Fig. 1). When the glass tube

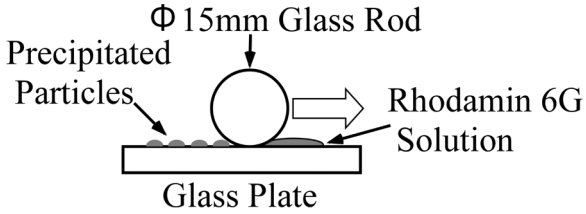

FIGURE 1 Schematic view showing the wetting/dewetting procedure to control the thickness of the ethanol solution of the Rh6G dye, which is accomplished by the pressing of a glass rod against a substrate surface whose hydrophilicity was controlled by a preceding ozone processing.

slid on the glass surface smoothly at 50 to 200 μm/s (controlled by DC servomotor), a very thin film of ethanol solution was formed. Then ethanol evaporated from this thin film and many small particles of rhodamine 6 G precipitated. The evaporation speed was determined by the thickness of the solution film that depended both on the hydrophilicity of the surface and on the spacing between the glass rod and the substrate. The evaporation speed should also depend on the temperature that was kept about 24 degrees (ambient). To raise the hydrophilicity of the surface, we irradiated the substrate with a 40 W low-pressure UV lamp under pure oxygen atmosphere. Photogenerated oxygen radicals were expected to dissolve the organic debris on the substrate into CO_2, H_2O, NO_2 and SO_2 gases. We used pure oxygen atmosphere in order to control the hydrophilicity easily: Since the oxygen absorbs the UV light efficiently, average ozone concentration should increase gradually in time and the surface chemical reaction was also expected at a moderate speed. Indeed the reaction speed decreased when the lamp was set more apart from the substrate.

Preparation of Dye Particles Embedded in a Polymer Film

Since tiny dye particles have large surface-area-to-volume ratio, they might suffer oxidation or other chemical reactions that will degrade their optical response. To suppress the possible photobleaching of surface-rich dye particles, transparent polymer films was formed at the same time as the dye particles precipitated so that the dye particles were embedded in a thin polymer film. Polymethylmethacrylate (PMMA) polymer pellet was first dissolved in chloroform at high concentration (30 mg/ml), and then small portion (50 μl) was mixed into rhodamine 6G ethanol solution (1 ml). Then this mixture was also used for wetting/dewetting procedure.

Optics to Observe the Near-Field-Excited Near-Field Fluorescence of Dye Particles

Dichroic mirror optics was incorporated in the near-field optical microscope (Fig. 2) in order to separate the specimen fluorescence from the excitation laser (CW Nd/YAG SHG modulated at 270 Hz). The specimen particle was optically excited with the near-field at the tip of the optical probe and the near-field component of the specimen fluorescence was collected with the same probe.

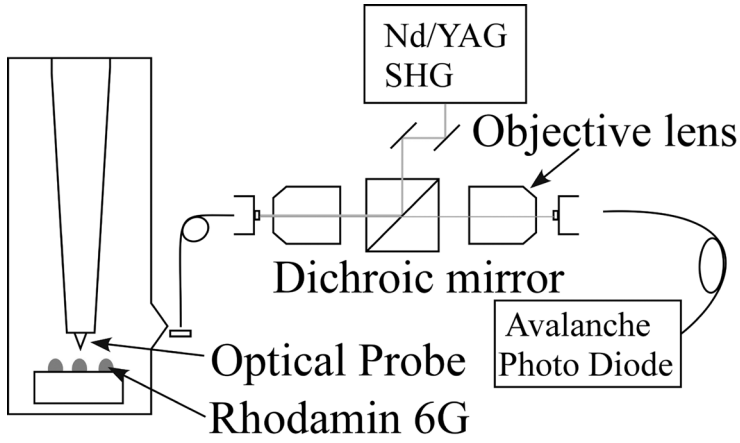

FIGURE 2 Optical setup to observe the near-field-excited near-field fluorescence. In this illumination/collection mode, the same optical probe are used both for photo-excitation and for fluorescence detection, the lights are separated on a basis of wavelength by a dichroic mirror and optical filters.

RESULTS AND DISCUSSIONS

Self-Assembled Arrays of Dye Particles

In the reflection image of an optical microscope (Fig. 3(a)), one can observe two types of particles, the larger ones with 2–5 μm diameter and the smaller ones with <1 μm diameter, arranged in a direction of glass rod movement. Note that no clustering of particles is present, which is one of the best characteristics of the present procedure.

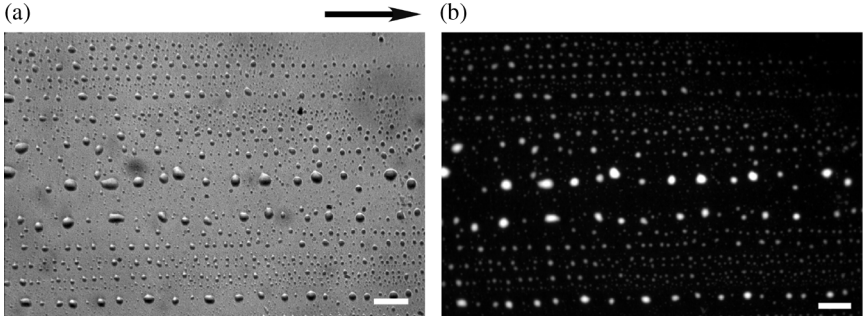

FIGURE 3 Optical microscope images of a Rh6G self-assembled array specimen. (a) The reflection image and (b) fluorescence image. Bars indicate 20 μm.

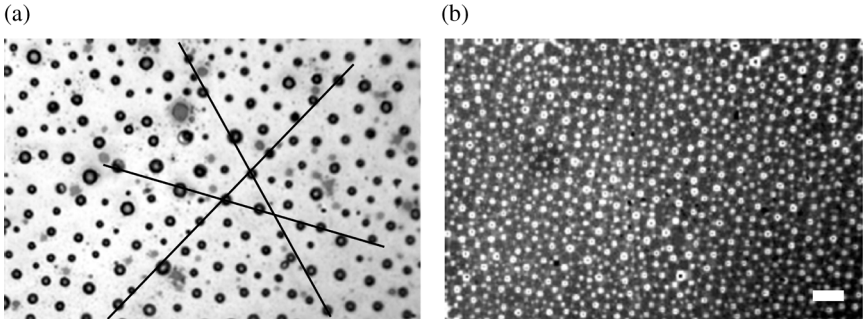

FIGURE 4 Optical microscope images of a Rh6G self-assembled array specimen. (a) Hexagonal-like arrangement is identified in some regions, (b) uniform distribution with similar inter-particle spacing.

It enables us to easily distinguish optical responses from separate particles and to perform the single particle analysis on a solid basis.

All the particles were made of rhodamine 6G, which is visualized in the epi-fluorescence image in Figure 3(b). Under another dewetting condition the particles showed a two-dimensional hexagonal-like arrangement in some regions (Fig. 4(a)), and other conditions lead to only an isotropic arrangement but with homogeneous inter-particle spacing (Fig. 4(b)).

Evaporating speed of the solvent had conspicuous effects on the appearance of the particle arrangement. Ethanol took more time to evaporate than chloroform did and it showed better arrangement of resultant dye particles.

Detailed mechanisms which governs the size and the spatial distribution of the precipitated particles aren't clear at present. However the spacing (let us denote it as $2r_p[\mu m]$) between the particles suggests that some competition of the particle growth should limit the particle size when it accumulates dye molecules from its surrounding region. Judging from the resulting spatial distribution, the initial precipitation core should have accumulated molecules from the surrounding region of radius r_p. If the thermal diffusion speed of the dye molecule becomes high, this r_p should become larger. On the other hand if the evaporation speed of the solvent becomes high, r_p would be expected to become smaller. If we raised the ambient temperature, both of the thermal diffusion speed and the evaporation speed would become higher and we couldn't predict the resulting behavior of r_p. Therefore we controlled the thickness of the solution via the hydrophilicity of the surface; the thinner is the thickness, the smaller would be r_p.

Near-Field Fluorescence of Dye Particles

When we introduced the second harmonic (532 nm) of Nd/YAG laser into the flat end of optical probe, we detected non-negligible fluorescence from the probe fiber. To minimize this background fluorescence we needed 1) to make the radius R of the focused laser spot less than that ω of the core region of the fiber: $R \geq \omega(= \lambda f/\pi\omega_0)$ and 2) to set the incident angle θ within the critical angle determined by the total reflection at the core/clad interface inside the fiber: $NA_{fiber} \geq \sin\theta$, where λ and ω_0 are wavelength and beam radius of the collimated laser, respectively, and f is the focal length of the coupling lens. These two conditions give $\frac{\lambda}{\pi R} \leq \frac{\omega_0}{f} \leq \frac{NA_{fiber}}{\sqrt{1-NA_{fiber}^2}}$, which is a severe condition to meet practically in selecting optimum coupling lens. Further we used a pure silica (undoped) optical fiber to introduce the laser and then coupled it to the probe fiber via FC-to-FC connector coupler to suppress the background from the fiber core itself. When we introduced the laser into a conventional single mode (SM) fiber it emitted a background of 200 mV while the pure silica fiber showed only 16 mV background (i.e., decreased down to 8%).

Using a pure silica fiber for coupling laser into we could manage to observe the near-field fluorescence from the separated particles using lockin detection (Fig. 5(a) and (b)). Both fluorescence images showed similar intense regions corresponding to the encircled bumps in surface topography (Fig. 5(c)). However other bumps in the topography didn't correspond to the intense fluorescence, indicating that they were non-fluorescing particles. Majority of the particles seemed to be in inactive state when we observed the region of more than 100

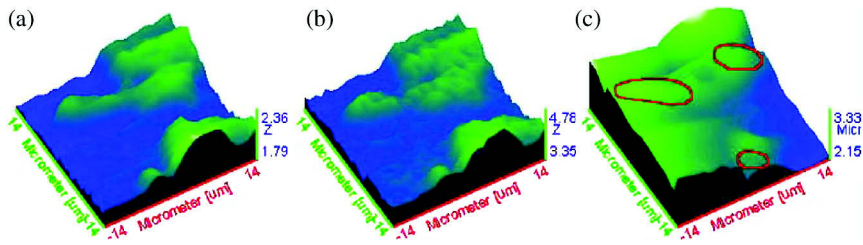

FIGURE 5 Near-field fluorescence of medium size particles within a Rh6G self-assembled array when the excitation Nd/YAG SHG CW laser was modulated by a 270 Hz rectangular wave (c) the topography. The phase of the detected lockin signal was shifted 45 degrees by our electronics, which brought about the similar images in (a) in-phase and (b) out-of-phase component, but only their difference has significance.

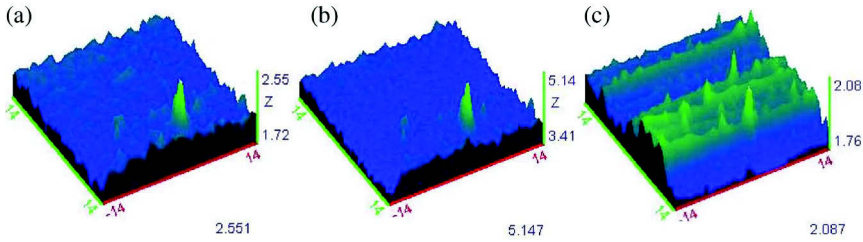

FIGURE 6 Near-field fluorescence of small particles within a Rh6G self-assembled array, (a) in-phase (b) out-of-phase component, and (c) the topography.

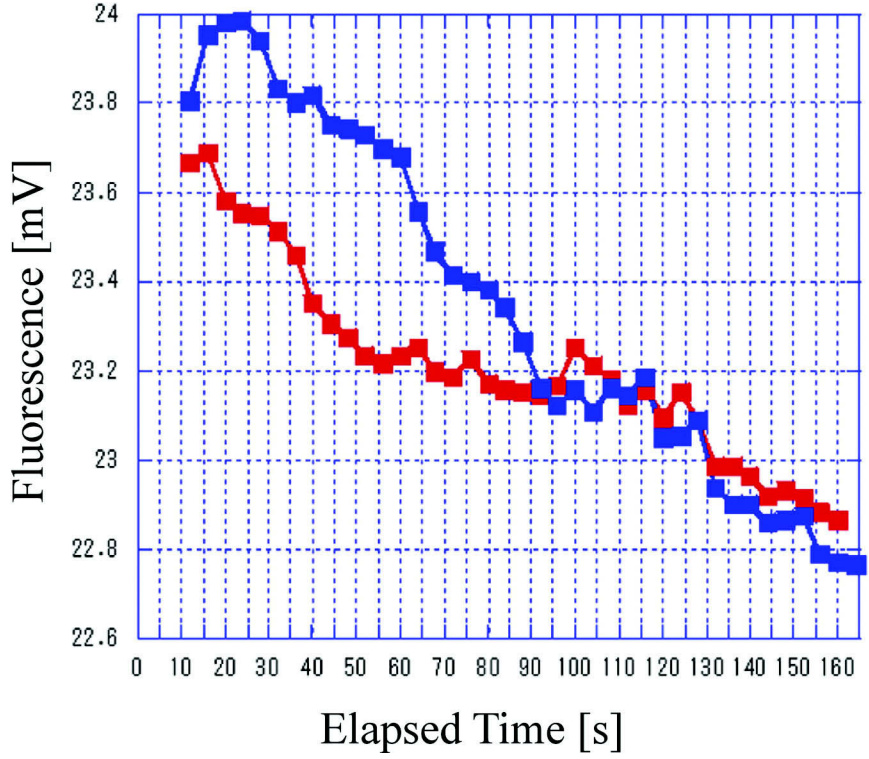

FIGURE 7 Long-term decay of the Rh6G near-field fluorescence upon laser exposure. Initially fluorescence signal was 1/20 of the background. Specimen was Rh6G large particles in a self-assembled array.

sub-micrometer particles as shown in Figure 6, although we scanned the area only once under photo-excitation to suppress the possible photo-bleaching of dye molecule. Our detection system had enough sensitivity because some particles of sub-micrometer size did show definite fluorescence over the background.

Therefore we should check the photobleaching of the dye. Figure 7 shows two example decay curves of near-field fluorescence of a larger particle in a self-assembled array. They showed a gradual decay in about a minute presumably due to photobleaching of the dye. To overcome this we tried to embed the specimen in a polymer film.

Dye Particles Embedded in a Polymer Film

The precipitated dye particles were successfully embedded in a thin PMMA film but they seemed to show a different arrangement (Fig. 8). Unidirectional alignment seems to be preferred in the polymer film embedded particles along the movement of solvent boundary while evaporation took place. Surrounding PMMA polymers may interfere the diffusion of the dye molecule, resulting in smaller particles of dye. Or the retraction of the solvent boundary itself,

FIGURE 8 Optical microscope image of Rh6G self-assembled array specimen embedded in a transparent polymer PMMA film.

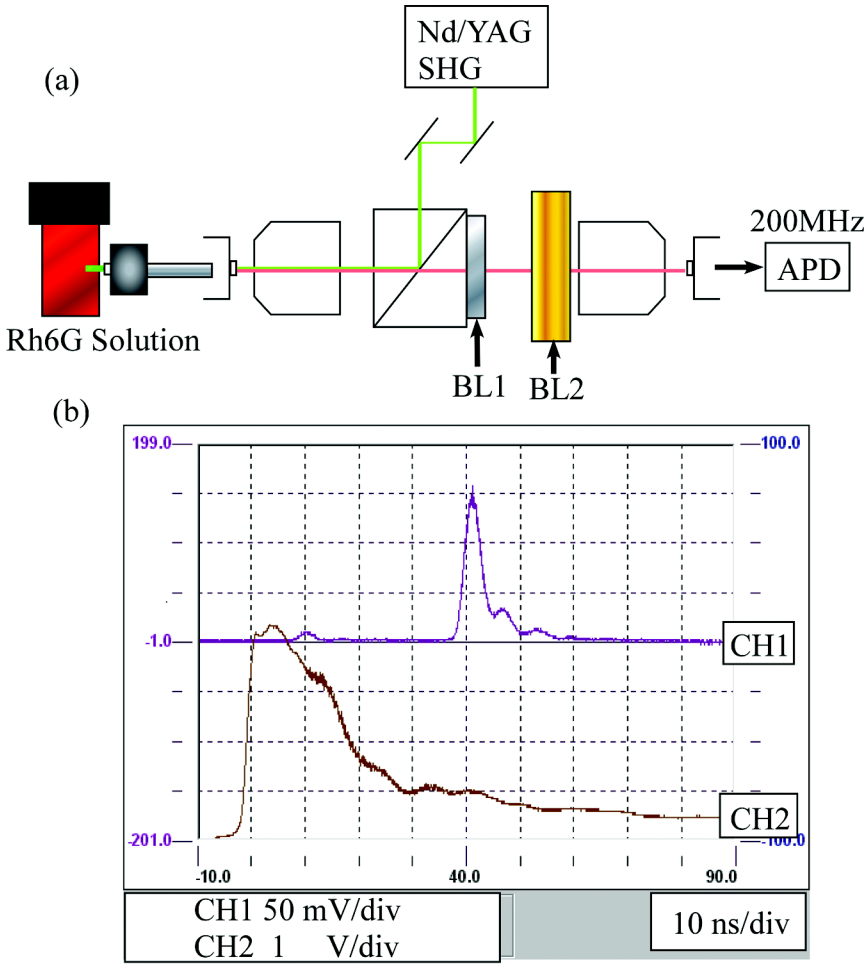

FIGURE 9 (a) Optical setup to observe time-resolved fluorescence using a Nd/YAG SHG pulse laser with 1 ns pulse width formed by a saturable absorber. Optical detection under high background was performed with high-speed APD using digital lockin amplifier. Excitation laser blocking filter was replaced with two sets of BL1 and BL2 to better suppress the background fluorescence. (b) Clear separation of the specimen fluorescence from the background fiber fluorescence based on the time difference along the optical path.

especially its velocity, might be modified by the viscosity of the polymers, which made the precipitation mechanism of the dye different between in the directions parallel and perpendicular to the solvent

boundary. Film thickness was found to be more than 1 μm, which made near-field study difficult.

Time-Resolved Study of Near-Field Fluorescence

We expect less photobleaching of the specimen when it is irradiated by short pulse laser. In this respect we used a diode-pumped passively Q-switched Nd/YAG SHG laser with ~1 ns pulse width and traced the fluorescence time course with about 10 ns time-response (even shorter for small signal) using ~1 ns response avalanche photodiode together with a 200 MHz preamplifier (Fig. 9(a)). In Figure 9(b), the background fiber fluorescence was only detected at 12 ns after the rising edge of an internal photodiode. Its origin was identified at the laser entry into the single-mode fiber judging from a delay time and also assured as becoming larger when the incident laser focused spot was positioned at the fiber clad. This is consistent with our previous arguments. The fluorescence peak from the Rh6G solution (a test specimen) was clearly resolved and detected at 30 ns after the background fluorescence that was expected from the fiber length 3 m and the light velocity within the silicate fiber core 20 cm/ns (index of refraction 1.5). The signal shows a decay time ~2 ns, but this might reflect the time-response of the APD for a small signal. The real fluorescence decay time might be shorter. Further averaging of the signal would be necessary to obtain a near-field fluorescence from tiny particles.

CONCLUSIONS

Separate sub-micrometer particles within the self-assembled arrays of organic dye were successfully identified in the near-field optical image. Some of the particles showed near-field-excited near-field fluorescence, whereas majority of the particles didn't show the fluorescence even in the first photo-excitation. The dye molecules within these particles might be in optically inactive state, which may be a result of oxidation by ambient oxygen, or they might be tightly coupled to the glass substrate to which emitted photons were leaked and weren't coupled to the probe.

REFERENCE

[1] Karthaus, O., Grasjo, L., Maruyama, N., & Shimomura, M. (1999). *Chaos.*, *9*, 308–314.