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Transfer of Dye Monolayers onto Silver Metal Films Formed by Photolysis of Silver Salt of Carboxymethylcellulose

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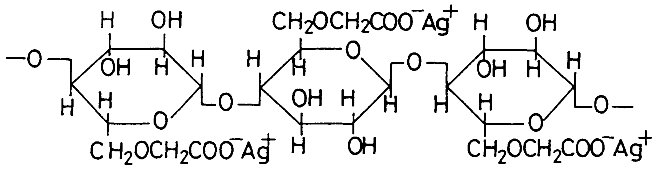
A bright silver mirror was formed by photolysis of silver salt of carboxymethylcellulose with 253.7 nm light. The silver metal film was proved to be useful for the substrate to deposit dye monolayers. Fluorescence quenching of rhodamine B on the silver metal film was interpreted in terms of excitation energy transfer.

Recently, fabrication of thin metal films by wet processes has attracted considerable attention.[1-4] We have studied photolysis of the silver salt films of high molecular weight carboxylic acids on the quartz plates.[5] On irradiating with UV light, the film surface finally changed into a bright silver mirror. Kuhn et al. have carried out pioneering works on dynamics of excited dye molecules in monolayer assemblies deposited at the metal surface.[6,7] In this study, we have attempted to deposit dye monolayers on the silver metal films formed by photolysis.



CMC Ag$^+$

The film of silver salt of carboxymethylcellulose (CMCAg$^+$) was prepared by using sodium salt of carboxymethylcellulose (Wako Chemicals) as a starting material.[8] The CMCAg$^+$ film, 1-5 µm in thickness, was exposed to 253.7 nm light from a 15W sterilization lamp (Toshiba) for about 8 h at 20-30 °C in wet air (relative humidity more than 70%) to form the silver metal films (CMCAg^M). The ORB:AA=1:9 monolayer was formed as before[9] by spreading the mixed solution of 0.3 mM N-ethyl-octadecylrhodamine B (ORB, Nippon Kanko Shikiso) and 2.7 mM arachidic acid (AA, Nakarai Chemicals) (1 M=1 mol dm^{-3}) in $CHCl_3$ on the aqueous subphase containing 0.3 mM $Ca(NO_3)_2$ at 16-19 °C and compressing until surface pressure reached about 30 mN/m. The (2×1) dye layers having two ORB:AA monolayers on one side of the plate, either CMCAg^M, CMCAg$^+$, or quartz, were fabricated by a vertical deposition technique.[9] After monolayer transfer, dye layers on one side of the plate exposing the quartz surface were wiped off. Absorption and fluorescence spectra of dye layers were measured at room temperature in air by using a UV-260 spectrophotometer (Shimadzu) and a 850 spectrofluorometer (Hitachi), respectively.

The variation of the absorption spectrum of the $CMCAg^+$ film with UV irradiation is given in Fig. 1. Before irradiation, the film was colorless and transparent in the visible range. A colloidal absorption band around 410 nm developed with irradiation. After 8 h, the irradiated surface changed into a bright silver mirror. The electrical resistance of the film was sharply decreased from about 10^{10} Ω at the beginning to less than 10^3 Ω. According to the observation of the morphology of the $CMCAg^+$ films by a high-resolution scanning electron microscope, the surface looked smooth before irradiation. After prolonged irradiation, the film surface was densely covered with colloidal silver particles (50-100 nm diameter). It appeared that the silver metal film is composed of the aggregates of colloidal silver particles.[10]

Typical fluorescence spectra of dye layers on all the plates are given in Fig. 2. The absorption spectra of dye layers on the $CMCAg^+$ and the quartz plates are shown in the inset. The monomer absorption band (M-band) at 565-570 nm and a shoulder around 520-525 nm of ORB agree with our former work.[9] The strong absorption of UV-visible light made it difficult to observe the absorption spectrum of dye layers on the $CMCAg^M$ plate. A distinct fluorescence peak of ORB around 600 nm[9] was observed for all the samples. The $CMCAg^+$ film was fluorescent in itself, showing a broad band around 500 nm. However, the fluorescence peak almost disappeared after 5 min irradiation. After subtraction of this contribution, the fluorescence intensity of dye layers on the $CMCAg^+$ plate was nearly equal to that on the quartz plate. When the $CMCAg^M$ plate was used instead of the quartz plate, the fluorescence intensity was reduced to less than 10%.

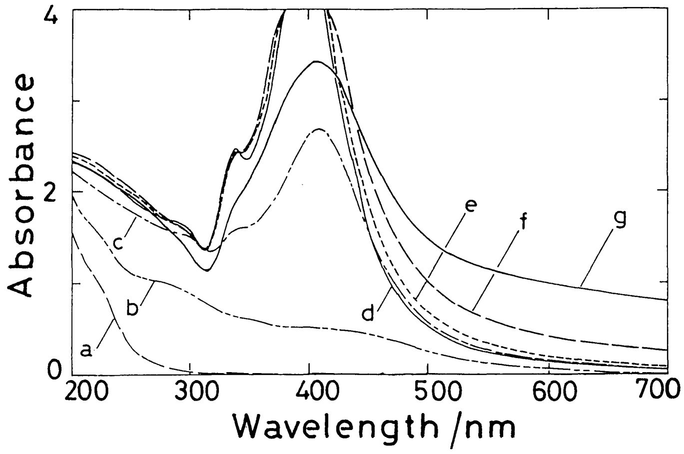


Fig. 1. Variations of the absorption spectrum of the $CMCAg^+$ film on the quartz plate. Irradiation time ; a: 0, b: 1, c:5, d:30, e:60, f: 120, g: 480 min.

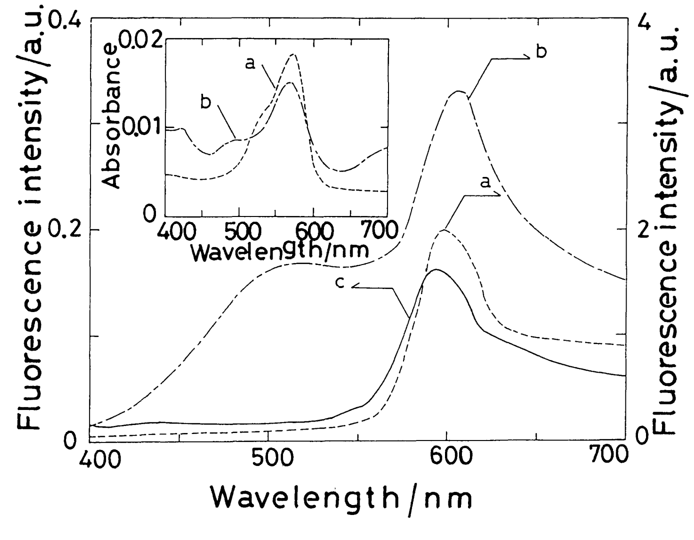


Fig. 2. Fluorescence spectra of (2×1) dye layers on the quartz (a), the $CMCAg^+$ (b) and the $CMCAg^M$ (c) plates. Molar mixing ratio of dye layers is ORB:AA=1:9. Excitation wavelength is 365 nm. Inset; Absorption spectra of (2×1) dye layers on the quartz (a) and the $CMCAg^+$ (b) plates.

To gain further insight, we fabricated the monolayer assemblies, [CMCAg^M/spacer/dye] and [CMCAg$^+$/spacer/dye], by using calcium arachidate (CaAA) monolayers as the spacer. To calibrate the variations in repeated sample preparations, we dissolved dye layers with $CHCl_3$ after fluorescence measurements and recorded the absorption spectra. The distance between the CMCAg^M film and dye layers, d, was estimated by assuming the thickness of the CaAA monolayer and the ORB monolayer to be 2.7 nm[9] and the height of the chromophore to be 0.3 nm. The relative fluorescence intensity, I, of the monolayer assembly as defined by the ratio of the observed fluorescence intensity at the peak around 600 nm to the absorbance at the M-band, is plotted versus d in Fig. 3. Similar data for the [CMCAg$^+$/spacer/dye] assembly are also included. The relative fluorescence intensity of the [CMCAg$^+$/spacer/dye] assembly is about 450 irrespective of d. On the other hand, I is increased with d in the [CMCAg^M/spacer/dye] assembly. Kuhn[7] and Chance et al.[11] analyzed energy transfer from an excited molecule to the metal films from the viewpoint of classical electrodynamics. With reference of those works, together with special features of the silver metal films in the [CMCAg^M/spacer/dye] assembly that an apparent thickness (0.1-0.5 μm)[5,10] is larger than d and that the surface would be partly covered with the very thin polymer film (average thickness L), an empirical relation between I and d has been introduced :

$$\frac{I}{I_0} = \left\{ 1 + \left(\frac{d_0}{d+L}\right)^n \right\}^{-1} \qquad (1)$$

Here, I and I_0 denote the fluorescence intensity in the presence and absence of the silver metal films, d_0 the distance (d+L), where I is one-half of I_0 and n the exponent. We have tentatively assumed d_0=26.5 nm, I_0=450, n=3 and examined the I versus d relation for varying L. A calculated I versus d curve for L=2.5 nm is given in Fig. 3. Although an agreement seems to be rather fortuitous, L of about 2.5 nm is not so unreasonable considering our current studies on electrical properties and Raman scattering of the silver metal films.[10] Fluorescence quenching in Fig. 3 would indicate energy transfer from an excited ORB

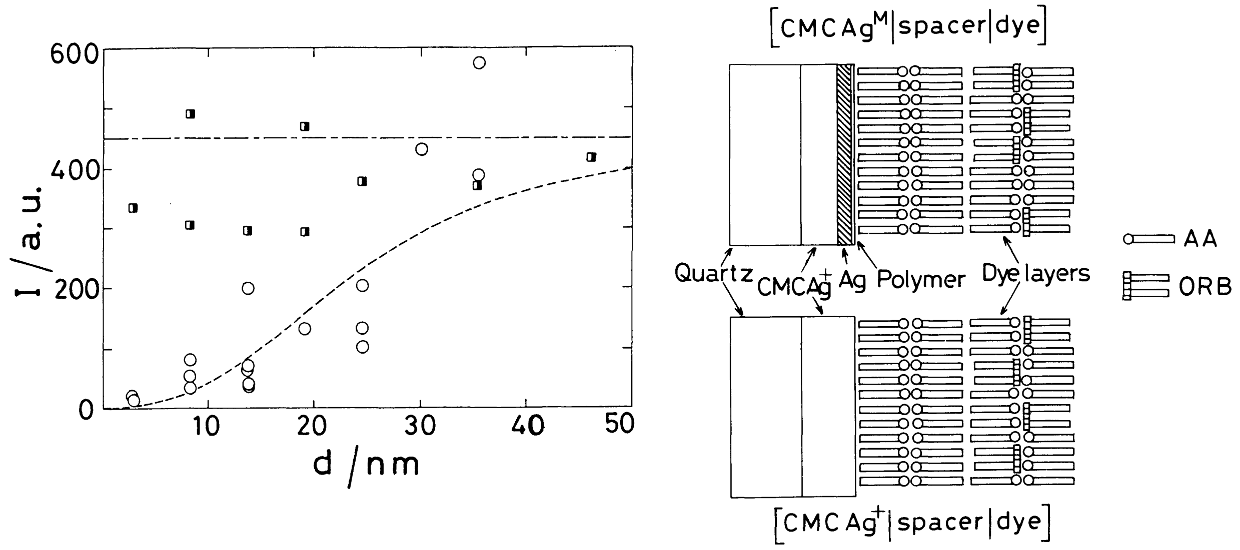


Fig. 3. Dependence of the relative fluorescence intensity, I, on the distance, d.
Excitation wavelength is 365 nm. ------ ; Theoretical curve given by Eq. 1.

molecule to the silver metal films.

It has been ordinary to employ an evaporated metal film on the quartz or the glass plate as the substrate for monolayer transfer.6) However, preparation of the good quality films by vacuum evaporation often requires elaborate techniques. One good point of the CMCAg^M film is an ease in fabrication. Another important aspect is a possibility to control aggregation state of photolytic silver by changing reaction conditions.5) We tested the silver metal films formed by photolysis of silver alginate and silver polymethacrylate. However, it turned out that those films were easily peeled off during monolayer transfer. At present, CMCAg^M is the only film that meets our requirements. The silver salt films of high molecular weight carboxylic acids irradiated with UV light are promising for the model system to study interaction of excited dye molecules with small silver particles in various aggregation states; clusters, colloids and bulk metals.12)

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