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Control of a Dye Formation Reaction in a Single Micrometer-Sized Oil-Droplet by Laser Trapping and Microelectrochemical Methods

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A dye formation reaction between 4-N,N-diethyl-2-methylquinonediimine and a phenol derivative at the oil-droplet/water interface was studied by a microelectrochemical method combined with laser trapping of an individual droplet in an oil-in-water emulsion system. The reaction in a single droplet with ≈ 10 μm diameter was shown to be controlled by the distance between the droplet and a microelectrode.

Chemical reactions in oil-in-water emulsions are in general very complicated since the reactions are governed by several factors such as mass transfer and diffusion-limited rate processes *in* and *across* the oil and water phases. In particular, since emulsions consist of various size of oil droplets, the results obtained by spatially-unresolved measurements are the sum or average of those for a number of the droplets and, therefore, such experiments do not provide a clear picture of primary chemical processes in emulsion systems. Furthermore, control of reactions in individual oil droplets based on conventional methods is far beyond possibility.

Previously, we reported that chemical reactions proceeding in individual microparticles dispersed in solution could be studied by spatially-resolved spectroscopy.[1-3] Although spectroscopy is certainly powerful enough to study chemical reactions in minute volume, the method is confined to samples with highly absorbing or fluorescent species. In order to extend studies on chemistry of individual particles, we developed an electrochemical system combined with laser trapping and spectroscopic methods (laser trapping-spectroscopy-electrochemistry system),[4] by which an individual microdroplet could be freely manipulated *on* or *in the vicinity of* a microelectrode to induce redox reactions in the droplet. Besides inducing redox reactions, an electrochemical technique is very suitable to study mass transfer processes, so that the present system will be highly potential to elucidate and control chemical reactions in individual droplets. In this letter, we report electrochemically-induced dye formation reactions at the oil-droplet/water interface and show that an efficiency of the reaction can be controlled by the distance (*l*) between the droplet and microelectrode.

As an oil-in-water emulsion, dibutyl phthalate (DBP; 1.17 g) containing a phenol derivative (C-Cp; 0.13 M (1 M = 1 mol dm^{-3})) was vigorously mixed with an aqueous solution of gelatin (12.5 wt %; 4.68 g) and sodium dodecylsulfate (5 wt %; 1.17 g) by a homogenizer (3000 rpm, 323 K, 5 min).[5] The emulsion (0.10 g)

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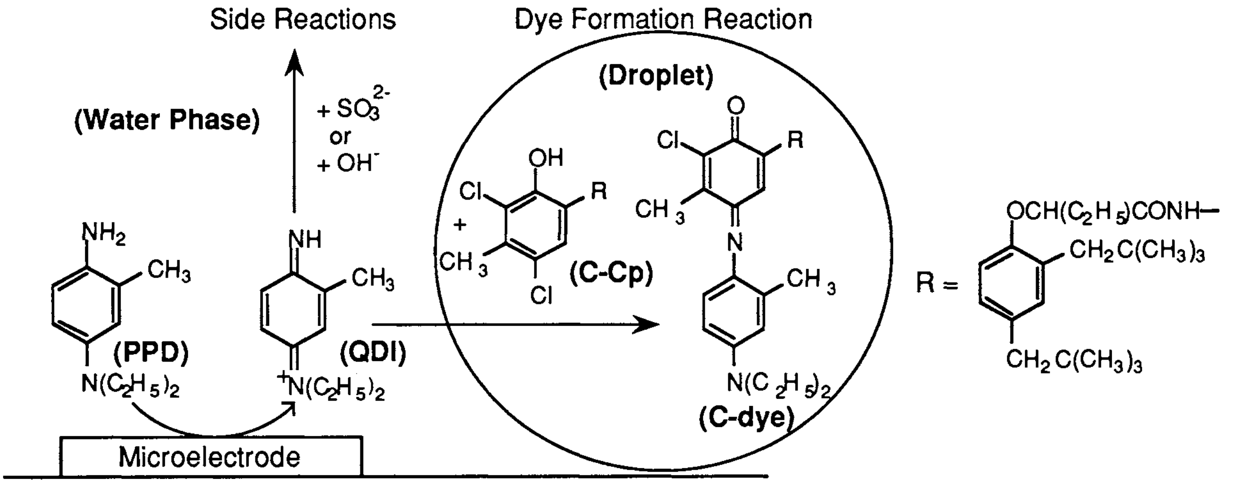

Fig. 1. Dye formation reaction at the droplet/water interface.

was dispersed in a K_2CO_3 (0.40 M) / $KHCO_3$ (0.32 M) buffer solution (9.90 g; pH=10) containing 4-N,N-diethyl-2-methylphenylenediamine (PPD; 5.0×10^{-3} M) and sodium sulfite (2.0×10^{-2} M). All measurements were performed at room temperature (295 - 296 K).

A dye formation reaction was studied by the laser trapping-spectroscopy-electrochemistry system.$^{4)}$ A 1064 nm beam (trapping beam) from a CW Nd^{3+}: YAG laser (Spectron, SL-903U) was introduced to an optical microscope (Nikon, Optiphoto XF) and focused ($\approx$ 1 μm) on a droplet through an objective lens (x 100). For absorption measurements,$^{6)}$ xenon flash pulses (Tokyo Instruments, XF80-60 , pulse duration $\approx$ 70 μs, 3 Hz) as a monitor light beam were led to the microscope coaxially with the 1064 nm beam, and focused ($\approx$ 6 μm) on the droplet. The monitor light beam (I_0 or I) was detected at 600 ± 160 nm by a photodiode array (Princeton Instruments, DSIDA). Au working (8 μm x 33 μm) and counter (0.2 mm x 3.5 mm) electrodes were fabricated on a sapphire plate by microlithography. A Ag/AgCl reference electrode was used throughout this study. The emulsion was poured onto the electrodes and covered with a glass plate, which was set on the microscope stage as an electrolytic cell. Electrochemical behavior was measured by a low current module (BAS, BAS100B).

The cyan-dye (C-dye) formation is assumed to proceed via a reaction scheme in Fig. 1 as reported previously for color developing processes in photographic emulsions.$^{7)}$ In the presence of OH^- (pH=10) and Na_2SO_3 (2×10^{-2} M) in the water phase, 4-N,N-diethyl-2-methylquinonediimine (QDI) produced by oxidation of PPD on the microelectrode undergoes deamination by OH^- and/or sulfonation by SO_3^{2-}. If QDI diffuses to the droplet/water interface and reacts with C-Cp, the C-dye is produced in the droplet. This implies that the C-dye formation in the droplet should be strongly dependent on the lifetime (τ) of QDI, since the dye formation competes with the deamination and/or sulfonation reactions in water. It has been reported that the deamination and sulfonation rates of N,N-diethylquinonediimine are $\approx 0.2\ s^{-1}$ and $\approx 2 \times 10^4\ M^{-1}s^{-1}$ at pH=10, respectively.$^{8)}$ Under the present condition of $[SO_3^{2-}] = 2.0 \times 10^{-2}$ M, τ of QDI is mainly governed by the sulfonation reaction and is estimated to be $\approx$ 3 ms, which corresponds to the diffusion length of QDI (Δ) to be $\approx$ 2 μm as calculated by the equation: $\Delta = (2D\tau)^{1/2}$, where the diffusion coefficient (D) for PPD ($\approx 5 \times 10^{-6}\ cm^2s^{-1}$, determined by cyclic voltammetry for a bulk solution) was used for the calculation. The Δ value and above discussion indicate that the C-dye formation can be controlled by l in μm-dimension. In photographs, development of color images

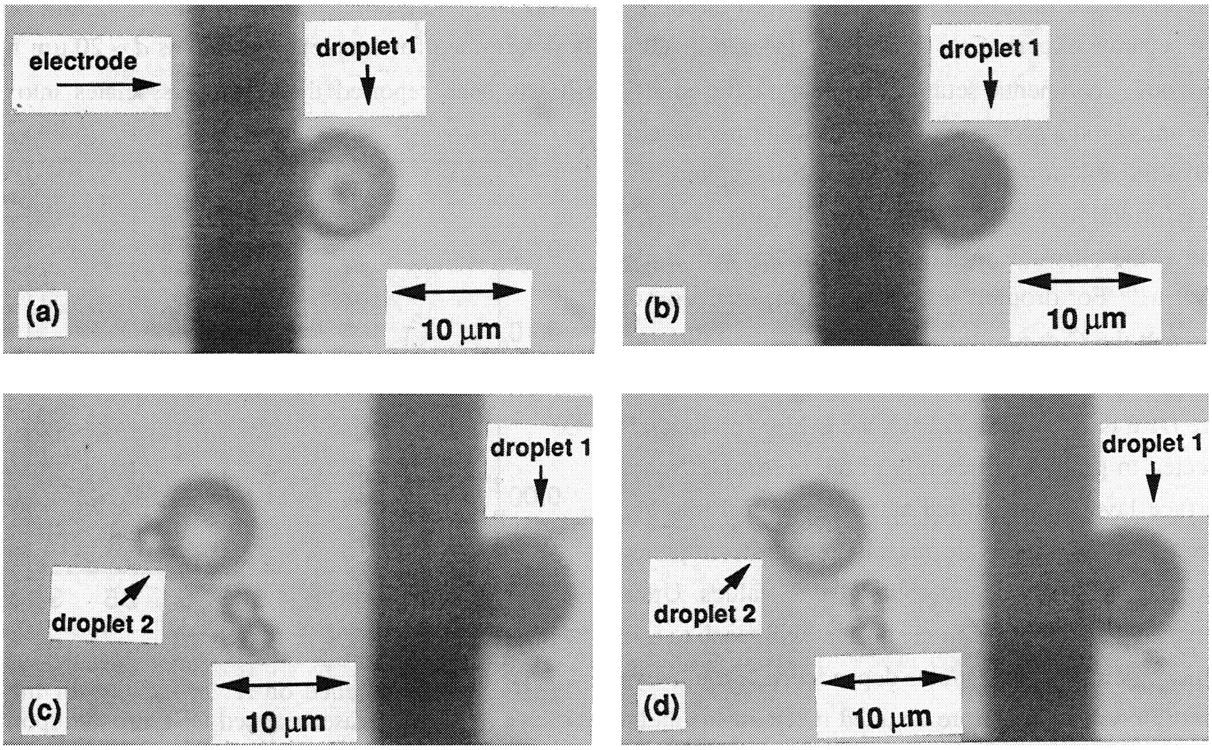

Fig. 2. Photographs of a laser-trapped DBP droplet(s) before (a and c) and after (b and d) 30 s electrolysis of PPD in water on the microelectrode.

depends on the distance between a silver halide particle and oil-droplets in a geletin film. The present study is of primary importance for basic understandings of photographic color development processes.

Photographs of a laser-trapped droplet(s) are shown in Fig. 2. Knowing the redox potential of PPD to be ≈ 30 mV, PPD in water was oxidized at 100 mV by a potential step method. When a droplet was placed at $l \approx 0$ μm (edge to edge distance between the electrode and droplet), the C-dye formation was saturated during the first 30 s (arrow 1 in Fig. 2(a) and (b)). Since Texter et al. have reported that PPD distributed in DBP droplets is not oxidized at $< \approx 400$ mV,$^{5)}$ the present result in Fig. 2(b) is ascribed to oxidation of PPD in the water phase and subsequent reaction of QDI with C-Cp in the droplet. The fast dye formation in the present system is due to short l. For $l \approx 9$ μm (arrow 2 in Fig. 2(c) and (d)), indeed, the dye formation was scarcely observed as expected from l (≈ 9 μm) >> Δ (≈ 2 μm). The dye formation was saturated during ≈ 90 s for $l \approx 6$ μm. Fig. 3 shows time (t) dependence of peak absorbance (A) of the C-dye (≈ 625 nm) in a droplet with ≈ 10 μm diameter (d). For $l \approx 0$ (Fig. 3(a)), A was saturated at ≈ 20 s after potential step, while that for $l \approx 9$ μm (Fig. 3(b)) was only 20% of the value for the droplet at $l \approx 0$ μm even after 30 s electrolysis. The results in Fig. 2 were proved by absorption spectroscopy on the individual droplets (Fig. 3).

If all C-Cp molecules in a droplet with $d \approx 10$ μm produce the C-dye upon reaction with QDI, A should be ≈ 4 as expected from the optical path length of 10 μm and the molar extinction coefficient of the C-dye (≈ 3×10^4 $M^{-1}cm^{-1}$ at 625 nm). However, A seems to be saturated at ≈ 0.16 as shown in Fig. 3(a). The monitor beam diameter (≈ 6 μm) is comparable with d, so that the actual optical path length for the droplet cannot be determined precisely and light scattering of the monitor beam by the droplet may influence A. Nonetheless, we suppose that the difference in A between the observed ($\approx$ 0.16) and predicted ($\approx$ 4) values is significant, since separate experiments indicate that A can be correctly determined for droplets as small as $d \approx 20$ μm by analogous experimental setup.[6)] In photographic emulsions, it has been reported that C-Cp dissociates into a C-Cp anion and a proton at the droplet/water interface in an alkaline solution, and a rate-determining step of the C-dye formation is coupling between QDI and the C-Cp anion at the oil/water interface for droplets with $d < \approx$ 0.25 μm.[7)] For droplets with $d \approx 10$ μm, diffusion of C-Cp and the C-dye to the droplet surface and interior, respectively, is limited by the viscosity in the droplet. Since DBP is viscous ($\approx$ 2 cPas), the C-Dye formation is expected to proceed efficiently at the oil-droplet/water interface layer in the initial stage of electrolysis. We suppose this is a possible reason for the discrepancy between the observed and calculated A values. Upon prolonged electrolysis, A in the droplet will reach to $\approx$ 4. Further studies on droplet-size dependence of the C-dye formation will reveal more detailed mechanisms and a possible role for the droplet/water interfacial reactions.

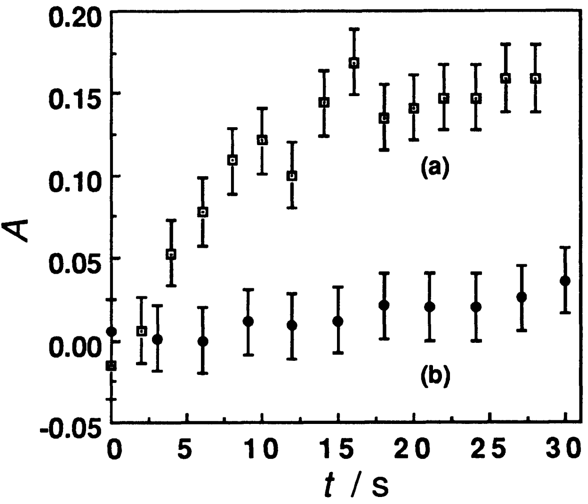

Fig. 3. t dependence on A at 625 nm of the C-dye in a single, laser-trapped DBP droplet upon electrolysis of PPD in water; (a) $l \approx 0$ μm, (b) $l \approx$ 9 μm.

In the present study, we demonstrated that chemical reactions in individual droplets coupled with electrode reactions in water could be controlled by the distance between the droplet and electrode. The present results clearly show potential means of the laser trapping-spectroscopy-electrochemistry system to induce and control chemical reactions in minute volume. Characteristic features of chemical reactions in micrometer domain will be revealed by such approaches and further studies are in progress in this project.

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