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Laser microchemistry

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Abstract - A new chemistry in μm small volumes is being opened by utilizing laser and related microfabrication techniques. Reaction microfields were prepared by laser ablation, scanning tunneling electrochemical microscope, and area-selective chemical vapor deposition. Utilizing optical pressure of lasers, microparticles such as microcapsules, liquid droplets, polymer latex particles, and so on can be manipulated, and photochemistry and spectroscopy of a single trapped particle is made possible. Fluorescence characterization of a microcapsule, lasing of a polymer latex particle, laser preparation of a polymer gel particle, photochemical construction of microstructure from particles were demonstrated. Photochemical dynamics in μm dimension is discussed for liquid droplet and liquid layer near the solid wall. To demonstrate a high potential of laser microchemistry, some trials for constructing a microchemical system are described.

INTRODUCTION

Nowadays a single atom or molecule can be observed and manipulated by scanning tunneling microscopy and related techniques. Chemists may control chemical reaction of one molecule, but we know that dynamic aspects of chemical reaction will not be studied by observing a single atom or molecule. In chemical reactions, molecules diffuse, encounter with each other, form complexes, react, and dissociate into products. A finite volume, extremely larger than nm-order molecular dimension, is necessary for molecules to undergo reactions. We have considered that μm/subμm volume is a crucial dimension for the studies on chemical reaction dynamics (ref. 1, 2). Only light is a potential means for energizing, interrogating, and controlling chemical reactions in small volumes, and it can be focused in a small spot of subμm.

To interrogate the reactions in short time domains, fast kinetic spectroscopy is indispensable and many molecules are necessary. Fluorescence and transient ultraviolet-visible absorption spectroscopy are fruitful, the latter of which requires about 10^7 excited states or reaction intermediates per μm^3. If their molar extinction coefficient is enough large (~10^5 $M^{-1}cm^{-1}$), it is possible to detect absorbance of 10^{-2} for μm path length.

To control chemical reactions in μm small domains, various kinds of method for preparing reaction microfields should be developed. Microlithography, chemical vapor deposition, scanning tunneling microscopy, optical microscopy, and photoactive molecules used in conjunction with lasers can be applied to prepare microfields on the surface of polymers, semiconductors, metals, and so forth by them. Spatial μm patterns are formed, and photofunctional molecules can be freely introduced on a small area.

To conduct reactions in μm dimensions manipulation method is strongly required. Particles, catalysts, and microcapsules containing reagents should be chosen, transferred, fixed at a certain position, and used in the reaction. By utilizing optical pressure of laser beam, we can now manipulate a single μm Brownian particle freely in three dimensional space under a microscope.

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On the basis of these technologies, it is possible to design and conduct chemical reactions in μm small volumes. It will contribute to understanding of reaction dynamics, creation of new functional materials, and development of microtechnologies such as microelectronics, microoptics, micromachine, and so forth. The chemistry in μm dimension thus realized by lasers is named here laser microchemistry. Some of our recent results are summarized and reviewed here.

PREPARATION OF MICROMETER REACTION FIELDS

Using various laser and fabrication techniques, μm sites with chemical functions are created on the materials surface. Simple observation of fabricated surface by microscopes is not enough, and their characterization is performed only by fluorescence and electronic absorption spectroscopy.

Irradiation of various materials with an intense laser pulse causes decomposition, melting, vaporization, and ejection of materials, leaving small holes. This is called laser ablation and has been used for microfabrication. The laser ablation is initiated by bond cleavage, so that radicals and ions should be left on the ablated surface of materials. If some molecules are contacted to this reactive surface, molecules are probably introduced to the surface. Micrometer resolution is easily attained in fabrication, so that simultaneous microfabrication and functionalization can be realized. Using a suitable optics, various micropatterns with specific molecules are formed, which is just preparation of reaction microfield. The idea was demonstrated for the first time for poly(methyl methacrylate) film (ref. 3).

The polymer film was irradiated in air through a meshmask with a 248 nm excimer laser. The etch depth and morphology was dependent upon laser intensity, so that chemical properties of ablated area and its neighborhood was different from each other. Immediately after irradiation the film was soaked in an aqueous solution of rhodamine B, leading to adsorption of the dye on the surface. This was confirmed by fluorescence observation under a microscope. It is very interesting that positive or negative fluorescent patterns can be prepared depending on the laser intensity.

According to conventional photochemistry of the polymer film in air, decompositions to fragments containing C = O, COOH, and OH groups or crosslinking of polymers are induced. The former oxidized derivatives may undergo reactions with dyes during soaking in solution, and the crosslinking, which is considered as a result of densely populated dissociated bonds, may suppress the plantation of dyes. Actually, rhodamine B fluorescence was observed on the ablated and adjacent areas under low and high intensity excitation, respectively, as shown in Fig. 1. Simultaneous microfabrication and functionalization of materials was thus demonstrated to be a fruitful means for preparing reaction field with μm dimension.

Micropattern was also formed by using scanning electrochemical microscope (SECM) in solution (ref. 4). Electrochemistry in the small volumes surrounded by the SECM tip and counter substrate electrode produces an oxidized or reduced compound, and it reacts with the substrate, giving a chemical modification. For introduction of organic molecules in organic polymers, the surface micromodification could be characterized by fluorescence spectroscopy with μm resolution. Preparation and detection of fluorescent micropatterns on conductive polymer films containing rhodamine 6G (R-6G) and methylviologen (MV^{+2}) are described.

The dye is fluorescent in the absence of MV^{+2}, while quenched in its presence. This is due to electron transfer and the basis of the present experiment. An ionic conducting polymer containing R-6G and MV^{+2} was coated on a platinum substrate (counter electrode) and scanned by a negatively biased tungsten tip of the SECM. The dye fluorescence was uniformly quenched, while the fluorescence recovered in the area where the tip was scanned. A typical example is shown in Fig. 2 where a fluorescent pattern of the letter M is obtained. The observed faradaic current indicates that redox reactions proceed in the film. The products are considered to have no quenching ability for R-6G, so that the fluorescence pattern in the scanned area was recovered. The resolution is dependent on the tip size and water content in the film, and improved to be subμm.

A conventional method to prepare micropatterns of organic molecules and polymers is to fabricate the films prepared in cm bulk dimension by microlithographic technique. On the contrary, we have proposed a unique approach for preparing micropatterns of organic polymers (ref. 5). The idea is to prepare an arbitrary micropattern of metals on a silicon wafer and to synthesize phthalocyanine only on the

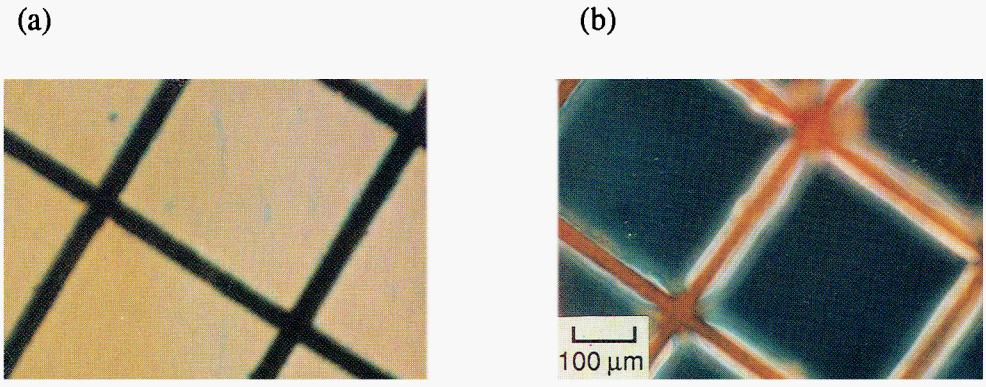

Fig. 1 Fluorescent micropattern of rhodamine B on laser ablated poly(methyl methacrylate) (a) 40 mJ/cm^2, 4000 pulses; (b) 570 mJ/cm^2, 700 pulses.

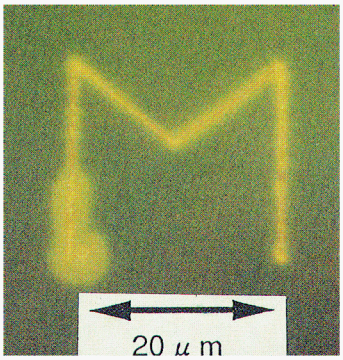

Fig. 2 Fluorescent micropattern of rhodamine 6G on conductive polymer. SECM tip was scanned at -4.0 V.

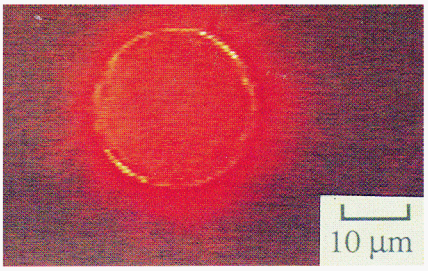

Fig. 5 Lasing of a laser-trapped, rhodamine B-doped poly(methyl methacrylate) particle in water. Intense ring-like emission is due to lasing.

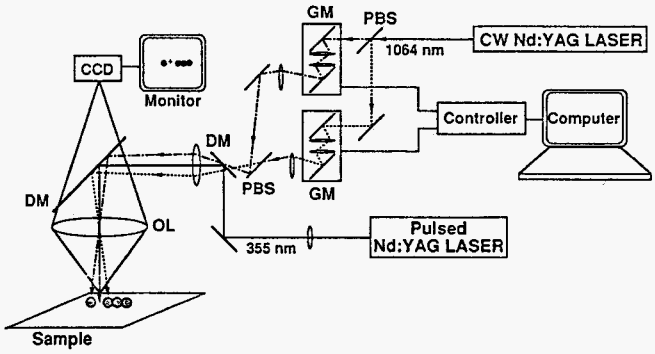

Fig. 3 A schematic diagram of a multi-beam laser scanning micromanipulation system.

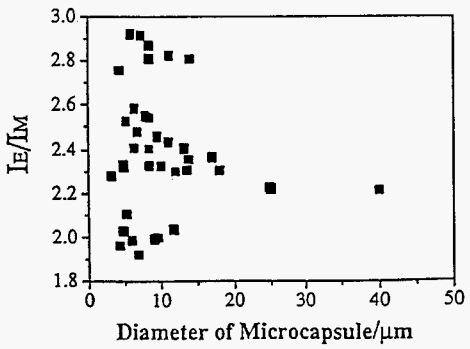

Fig. 4 Excimer-monomer florescence intensity ratio of pyrene/toluene in a single microcapsule as a function of its diameter.

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micropattern. Copper films were patterned on silicon wafer by photolithography and wet etching techniques. The silicon-copper substrate was sealed in a glass tube with 1,2,4,5-tetracyanobenzene and heated at different temperatures. Around 200 °C, selective chemical vapor deposition on the pattern was achieved, and copper phthalocyanine thin films were formed only on it. If the molar ratio of 1,2,4,5-tetracyanobenzene to copper is adjusted well, the copper base was completely changed to copper phthalocyanine. By thermal annealing the film was converted to its polymer, and the chemical and physical properties were greatly improved. The area-selective chemical vapor deposition was also performed on insulating and optically transparent materials. Phthalocyanine and its polymers are photoactive, sensing, and semiconductive materials, so that this is a promising way to fabricate and arrange chemical reaction microfields on various surfaces.

CHEMISTRY OF A SINGLE MICROSPHERE

Microspheres such as polymer particles, microcapsules, liquid droplets, microcrystals, catalysts, and colloids are in μm dimension and very interesting targets for laser microchemistry. Although techniques for characterizing them have been advanced greatly, one difficult problem not solved until now is to manipulate a single particle. Structures, properties, and reactions of microsphere systems are always analyzed and considered on the basis of experimental data statistically averaged. By utilizing optical pressure of lasers, Ashkin demonstrated for the first time to trap a single particle (ref. 6). Recently we have introduced this laser trapping technique and combined it with spectroscopy, photochemistry, fabrication, and established as a new tool for chemistry of a single microsphere (ref. 7, 8, 9).

When a Brownian microsphere in solution is irradiated by a focused laser beam under a microscope, the microsphere can be trapped at the focal point against thermal fluctuation. This is realized only when the following conditions are satisfied; (i) the refractive index of the particle is larger than that of the medium, (ii) a spherical shape is favored, (iii) laser light is sufficiently intense, and (iv) light is focused into a small spot with a lens of large NA value. The 1064 nm CW YAG laser was used for trapping, and the beam was arbitrarily scanned by galvano mirrors. A laser scanning micromanipulation system is schematically shown in Fig. 3. In addition to two trapping beams, the ps or ns UV laser pulse was introduced for exciting the trapped particle. Fluorescence and absorption spectral measurements, photochemical reactions, and fabrications are now possible for each microsphere.

Microcapsules have unique geometrical structures of resin wall with an inner solution and are widely used in printing materials, drug delivery systems, and so on. Photochemical and photophysical processes occurring in a single microcapsule can be measured by our space- and time-resolved fluorescence spectroscopy (ref. 10). Melamine resin microcapsules containing toluene solution of pyrene were prepared, and pyrene excimer formation dynamics was measured and analyzed. For high concentration of pyrene, both monomer and excimer fluorescence was observed, and their relative intensity ratio was examined as a function of the microcapsule diameter. As shown in Fig. 4 the ratio shows a large scatter for the capsules with the diameter smaller than 20 μm, while the fluorescence intensity ratio for the larger capsules was close to that of the bulk mother solution. Fluorescence dynamics in each microcapsule could be analyzed well with the Birks kinetics model. The rate constants of excimer formation and dissociation processes were independent upon the diameter. This means that the inner toluene solution is quite similar to the bulk solution in dynamical properties and the effective concentration is scattered for each capsule. The concentration distribution of pyrene between the capsules could be determined during the preparation processes of the capsules. An evaporation rate, microcrystallization of pyrene, partition of water, polymerization process, and so forth are the factors affecting the present behavior. An interesting study on an individual microcapsule is started.

Exciting dyes in the particle with intense laser lights, the lasing behavior of the laser-trapped particle was observed for the first time (ref. 11, 12). Rhodamine B or 640 was doped in poly(methyl methacrylate) particles with a tens of μm diameter, and its individual particle was trapped and excited. Fig. 5 gives an intense lasing emission near the particle-water boundary. Since the refractive index of the trapped particle is larger than that of the surrounding solution, optical feedback operates under the total internal reflection at the boundary. Since the emission leaks toward the tangents of the spherical cavity, intense ring-like emission was observed. As shown in Fig. 6, a simple fluorescence spectrum with a broad and structureless band was observed at low excitation, while distinct resonance peaks appeared with increased laser intensity. The spacing between the resonant peaks is given as a function of the wavelength, particle diameter, and refractive indices.

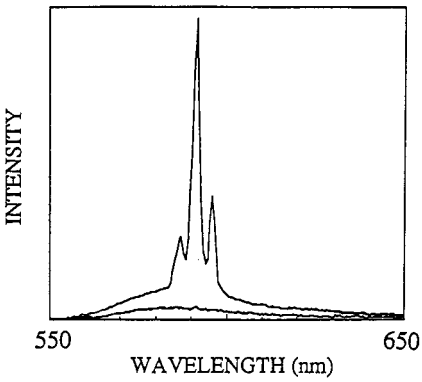

Fig. 6 Emission spectra of laser-trapped, rhodamine B-doped poly(methyl methacrylate) particle in water.

Our advantage is a high potential to manipulate the lasing particle in solution freely in three dimensional space. One application is to use the lasing particle for spectroscopy. It is considered that electronic absorption spectra just inside or outside the particle can be measured, since the whispering-gallery mode is realized under the present total internal reflection condition. Another application will be a scanning photon tunneling microscope for probing surface morphology. Since lasing in a particle is based on optical feedback in the spherical cavity, a close approach of nonlasing particle to lasing one disturbs the cavity condition. Namely, photon leakage is induced and the Q-value is changed. Independent manipulation of the two particles makes it possible to adjust the interparticle distance. Thus, the morphology of surface will be observed. Simultaneous optical trapping and lasing of polymeric particles will be a useful technique for chemistry of a single particle.

Not only is it possible to characterize a single particle by spectroscopy but also to prepare a particle under a microscope is possible. The idea is based on a thermally induced phase transition of poly(N-isopropylacrylamide) solution (ref. 13). Aqueous homogeneous polymer solution was irradiated by the CW YAG laser (1064 nm), leading to the temperature rise. It is well known that gel phase appears above 31 °C, and actually a μm order particle was observed immediately after switching on the laser. The growing rate and the equilibrium size of the particle depend upon laser power, temperature, and concentration of the polymer. Switching off the laser the particle disappears quickly because the local temperature is lowered. The manipulation of the prepared single microsphere was very easy, so that we can create a single particle in solution at any time, transfer it to any position, and extinguish it in solution. Formation and disappearance processes of a single gel particle, its structures and properties, and applications are being studied.

By means of photopolymerization reactions laser-manipulated plural particles can be chemically combined with each other leading to a construction of a microstructure (ref. 14). Polystyrene (PSt) particles with a 1 μm diameter were dispersed in ethylene glycol solution of acrylic acid, N,N-methylene bisacrylamide, and Darocure 1116. Manipulating independently two particles with two trapping laser beams and contacting them firmly, the boundary area was irradiated by the 3rd harmonic (355 nm) of ps YAG laser. Photoinitiator and polymerizable monomers undergo reactions, rendering chemical binding of two particles. The stuck particles can be trapped in three dimensional space with a single trapping beam, so that the second trapping beam was used to catch the third particle and to contact it to the stuck pair. Then, again photoirradiation of the boundary area resulted in adhesion of three particles. The repetitive manipulation and photopolymerization makes it possible to construct any kind of microstructure from polymeric microspheres in noncontact and nondestructive ways.

PHOTOCHEMICAL DYNAMICS IN MICROMETER SMALL VOLUMES

Chemical reactions in μm small volumes are expected to show some new aspects compared to the bulk, however, such an experiment has been scarce. The first trial was given for interface layers of liquids near the solid wall. By applying time-resolved total internal reflection fluorescence spectroscopy, fluorescence dynamics was studied for coumarin 460 in 1-butanol and 1-naphthol in water (ref. 15). The fluorescence spectra and rise and decay dynamics at the interface were measured by changing the penetration depth of the evanescent excitation pulse. The evanescent wave excites only the interface layer with thickness less than 100 nm, and the fluorescence was detected and compared with that of the bulk.

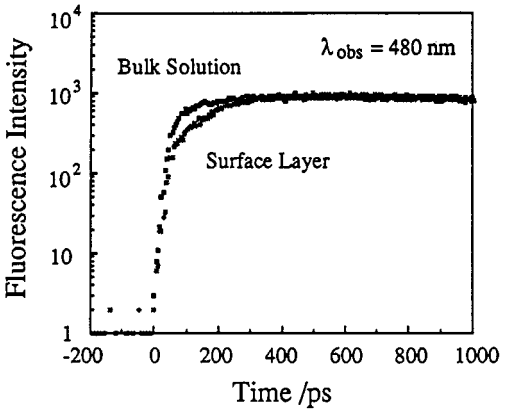

Fig. 7 Fluorescence rise curves of coumarin 460 on 1-butanol.

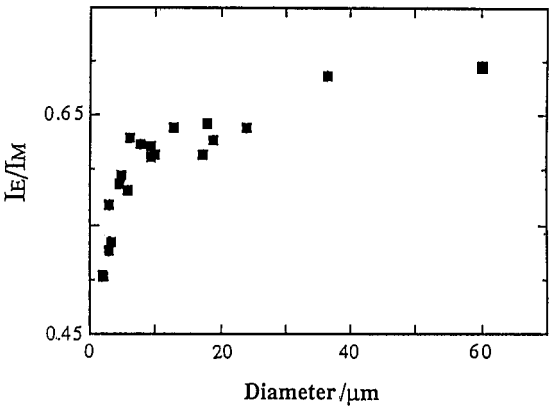

Fig. 8 Excimer-monomer fluorescence intensity ratio of a single paraffin droplet as a function of its diameter.

Coumarin 460 and 1-naphthol show a Stokes shift, and its time-dependent shift to the long wavelength was shown in the time-resolved fluorescence spectra, which are due to solvent reorientation and proton transfer processes. A difference is clearly demonstrated in the coumarin fluorescence rise curves as in Fig. 7. A similar behavior was observed for 1-naphthol in water whose fluorescence decay became slower as the penetration depth was decreased. The results indicate that both solvation dynamics and proton transfer process in the interface layer occur more slowly than those of the bulk.

Such characteristics of small volumes in liquid was also confirmed for a single liquid droplet in solution (ref. 16). An individual μm droplet in water was manipulated freely by the trapping laser beam, and the fluorescence spectra were measured as a function of the droplet size. Monomer and excimer fluorescence intensity ratio shows a large scatter for toluene and benzylalcohol droplet. On the other hand, the I_E/I_M value decreases for the paraffin droplet with the diameter below 10 μm as in Fig. 8. Similar results were also observed for silicon oil droplet.

One explanation is to assume that the pyrene solubility is dependent of the droplet size. Namely, for the small droplet, partition of water molecules into the paraffin may reduce solubility of pyrene, rendering a decrease in I_E/I_M. According to the simple estimation, the surface layer (surface area x molecular dimension) is negligibly small compared to the volume for the 10 μm droplet. Therefore, this explanation seems not to hold. Another possible origin is the μm size effect on the viscosity in minute liquid droplets. The smaller the droplet, the more viscous the solution. We consider that mutual association and/or orientation of liquid paraffin molecules at the interface results in a characteristic property, and it lasts to subμm order depth. Namely, the smaller the diameter of a droplet, the larger the contribution of such surface association/orientation to the solution viscosity in a droplet.

All these phenomena are given in the solution where mutual interactions of solvent molecules are appreciable. Hydrogen bonding and association of long chain molecules are the origin extending the interface effect to subμm. We consider that photochemical dynamics in these dimensions is characteristic and general.

TOWARD MICROPHOTOCONVERSION SYSTEM

A well designed combination of chemical processes in μm volumes will lead to a promising chemical system where high selectivity and high yield will be attained. It is preferable that reaction microfields are spatially arranged and reactions are conducted sequentially along the array of the microfields. To explore such a system, some trials for examining effects of geometrical arrangements of reaction microfields and for utilizing microdroplets in the microfields are started.

The first example is that photochemical processes can be controlled not only by applied potential but also by spatial arrangement of microelectrode (ref. 17). The system was tris(2,2-bipyridine) ruthenium (II) on interdigitated microarray semiconductor electrodes. Electron transfer processes from excited

ruthenium complex to the electrode (~100 μm long x 10 μm wide x ~0.2 μm height) in aqueous electrolyte solution were observed as a photocurrent at a suitable electrode potential. It is very interesting that the electron transfer yield was increased by adjusting the potential of the adjacent electrode which was not involved directly in electron transfer. This suggests that a geometrical arrangement of electrodes is crucial, which may be due to cyclic oxidation-reduction reactions.

The second example is to utilize a single liquid droplet in the chemical system. We chose a Brownian droplet in solution, to fix it on the microelectrode, and to measure the current (ref. 18). The system was ferrocene and 9,10-diphenylanthracene in oil droplets dispersed in water, and one droplet was manipulated and contacted to the electrode. Adjusting the electrode potential, ferrocene was electrolysed, leading to a recovery of 9,10-diphenylanthracene fluorescence. As ferrocene is a good quencher, the fluorescence analysis of each droplet will give an information of reaction process.

Arranging such reaction microfields spatially and conducting the reactions on them, we will construct a chemical reaction system with high selectively and high efficiency. The integrated chemical system is named microphotoconversion system which will demonstrate a high potential of laser microchemistry (ref. 1, 2, 19, 20).

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