Laser Manipulation and Ablation of a Single Microcapsule in Water

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Abstract: Laser manipulation and ablation of a single microcapsule containing a pyrene/toluene solution were demonstrated for the first time. Irradiation of an individual capsule by a focused (~1 μm) laser beam from a CW Nd^{3+}:YAG laser (1064 nm) enabled us three-dimensional optical manipulation of the capsule in water. When a laser-trapped microcapsule was further irradiated by a 355-nm laser pulse (pulse width ~7 ns), deformation or ablative decomposition of the capsule was observed depending on the pulsed-laser intensity. The pyrene/toluene droplet ejected from the capsule upon laser ablation was shown to be tweezered by the 1064-nm laser beam. Spectroscopic characterization of individual capsules and droplets was achieved by a laser trapping–spectroscopy technique. Ablation mechanism was also discussed in terms of the pyrene concentration dependence of the ablation threshold energy.

Introduction

When a laser beam is focused on a micrometer-order particle in solution, the particle can be optically manipulated along any direction,[2-5] and indeed, various particles such as polymer beads,[2,4,6] silica gels,[4] biocells,[5,7,8] and so forth[9,10] have been reported to be optically tweezered in water. This particular phenomenon of "*laser trapping*" was experimentally proved by A. Ashkin in 1970 for the first time,[2] and the theoretical model has been also given by his research group.[2-5] Laser trapping is essentially based on refraction of a laser beam by a dielectric particle. Namely, when a laser beam is refracted through a particle, the radiation force is exerted to the particle in the opposite direction of the light momentum change. If the refractive index of a particle (n_P) is higher than that of the surrounding medium (n_M), the radiation force directs toward the high-intensity region of the laser beam and a particle is optically "*trapped*" in the vicinity of the focal point of the laser beam.[2-5] Steering of the laser beam therefore leads to three-dimensional optical manipulation of a particle.

Nondestructive and noncontact optical manipulation of individual small particles in thermal Brownian motion is expected to play an important role in various fields of chemistry. Nonetheless, application of the laser-trapping technique to chemistry has never been explored since the laser-trapping phenomenon itself does not involve any chemistry. To induce chemical reaction in a laser-trapped particle, we recently developed a laser trapping–spectroscopy–ablation system and reported a new technique of three-dimensional manipulation, spectroscopic characterization, and microfabrication of an individual small particle in solution.[6,10-12] Spectroscopic characterization of a particle has been done in a nanosecond[6] to picosecond[13] time regime. Also, we demonstrated that a submicrometer hole could be fabricated on a single polymer latex particle with its diameter of 2–8 μm by laser trapping–ablation.[6,10] Clearly, the technique is promising to elucidate chemical/physical processes occurring in small particles as well as to fabricate an individual particle.

Among various small particles, microcapsules are very unique for their three-dimensional structure and are widely used in drug delivery, controlled drug release, and fine printing systems.[14,15] Since a variety of reagents can be encapsulated in polymeric resin, furthermore, microcapsules will provide various basic and industrial applications. For example, if we can manipulate a single microcapsule and decompose the resin wall arbitrarily in three-dimensional space, site-selective chemical modification/functionalization of the surface of microelectrodes, LSI circuits, and so on will be possible by an appropriate choice of the content in the capsule. We expect that laser manipulation and ablation of a microcapsule will be a novel mean for these applications. To test such possibilities, we explored laser trapping–ablation of a single microcapsule in water.

Experimental Section

Laser Trapping–Nanosecond Spectroscopy–Ablation System. A block diagram of the laser system employed in this study is shown in Figure 1. For laser trapping of a micrometer-order particle to be attained, a trapping laser beam should be focused into a wavelength-order spot. Furthermore, the particle to be trapped should be transparent at the wavelength of the incident trapping laser beam. To satisfy these conditions, a 1064-nm laser beam from a CW Nd^{3+}:YAG laser (Spectron SL-903U) was used as the laser-trapping source and was focused into a ~1-μm spot through an oil-immersion objective lens (OL, mangification ×100, numerical aperture, 1.30) of an optical microscope (Nikon Optiphoto XF). Trapping behavior was monitored by photographs or a CCD-TV monitor set equipped to the microscope. A sample solution placed between two glass plates was set on a three-dimensional scanning stage of the microscope.

For nanosecond spectroscopy or ablation of a laser-trapped particle, the third harmonics of a Q-switched pulsed Nd^{3+}:YAG laser (Quanta Ray, DCR-II, 355 nm, pulse width ~7 ns) was employed as an excitation light source. To match the focal points of both trapping and excitation laser beams in the sample solution, two laser beams were introduced coaxially into the microscope by using dichroic mirrors (DM1 and DM2) as schematically shown in Figure 1. Fluorescence from the sample solution was collected by OL and was analyzed by a polychromator (McPherson 2035, 150 G/mm) and a gated microchannel plate/photodiode array detector (Princeton Instruments, a D/SIDA-700G(B) detector, a FG-100 gate pulser, and a ST-110P controller). Timing between the pulsed laser and the detector was controlled by a digital delay generator (Stanford Research System Inc., DG-535). The pulsed-laser intensity at 355 nm was appropriately attenuated by a ND filter(s) before introducing the laser beam into the microscope. The trapping and ex-

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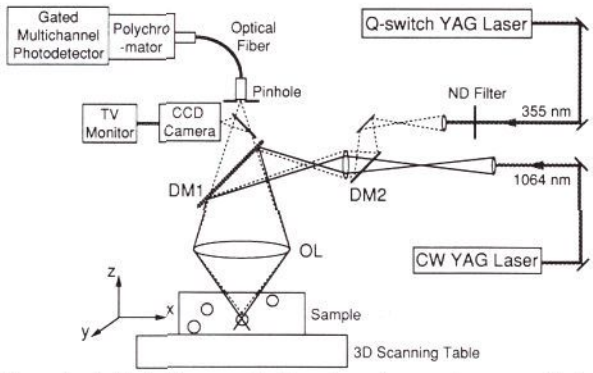

Figure 1. A block diagram of a laser trapping–spectroscopy–ablation system. OL, DM, and ND are an objective lens, a dichroic mirror, and a neutral density filter, respectively.

citation laser intensities irradiated into the sample solution under the microscope were determined as reported elsewhere.[10] Laser ablation of the microcapsule reported here was performed by single-shot pulsed-laser (355 nm) irradiation unless otherwise noted.

Preparation of Microcapsules. A mixture of acacia (3.5 g in 70 mL of water), pyrene in toluene (8.1×10^{-3}, 1.0×10^{-2}, or 0.11 M; 5 mL), and an aqueous solution (30 mL) of melamine (4.7×10^{-3} mol) and formaldehyde (1.4×10^{-2} mol) was vigorously stirred by a homogenizer for 15 min at room temperature after adjusting the solution pH to 4–5 with phosphoric acid. The mixture was transferred to a 100-mL round-bottom flask, and ammonium sulfate ($\sim 1 \times 10^{-2}$ mol) was added into the mixture. The reaction was allowed to stand for a further 2 h at 55 °C under mild stirring. Microcapsules containing toluene alone were also prepared as a reference sample. For spectroscopic measurements, it is desirable to purify or wash the microcapsules. However, when the microcapsules prepared were washed with enough water, the capsules coagulated with each other and were not homogeneously redispersed in pure water. In the present study, since no detectable emission was observed from the aqueous phase of the reaction mixture, we used the reaction mixture as the sample solution without any purification.

Results and Discussion

Laser Manipulation of a Single Microcapsule in Water. Three-dimensional laser manipulation of a single pyrene/toluene microcapsule in water was easily attained by illuminating the 1064-nm laser beam on the capsule. Figure 2 proves laser manipulation of the capsule (diameter ~ 7 μm) along the lateral (X or Y) direction of the microscope stage. To distinguish the capsule from spherical toluene droplets (either unencapsulated or ejected from decomposed capsules), we trapped the nonspherical capsule. In Figure 2, the capsule shown by the arrow is laser-trapped while other capsules were not illuminated by the laser beam. Untrapped capsules move along the X (Figure 2a) or Y (Figure 2b) direction with the microscope stage whereas the trapped capsule remains at the same position. We succeeded in laser manipulation of the capsule along the laser beam axis (Z direction) as well. Besides microcapsules, polymer latex particles (poly(methyl methacrylate) and polystyrene in water, ethylene glycol, or diethylene glycol), various liquid droplets in water, titanium dioxide in water, and so forth have been demonstrated to be similarly manipulated by the focused 1064-nm laser beam.[10]

For laser trapping of a particle to be attained, the refractive index of a particle (n_P) should be higher than that of the surrounding medium (n_M).[2-5] As a typical example, a poly(methyl methacrylate) (PMMA, $n_P = 1.49$)[16] latex particle can be easily manipulated optically in lower refractive index medium, water ($n_M = 1.33$).[17] In the present case, although precise n_P of the capsule is unknown, the value will be very close to n_P of toluene (1.50).[17] n_P of the capsule is thus expected to be higher than that of water, satisfying the condition of $n_P > n_M$. The shape of polymer latex particles is spherical while the microcapsule possesses the three-dimensional structure with the thin melamine resin wall and

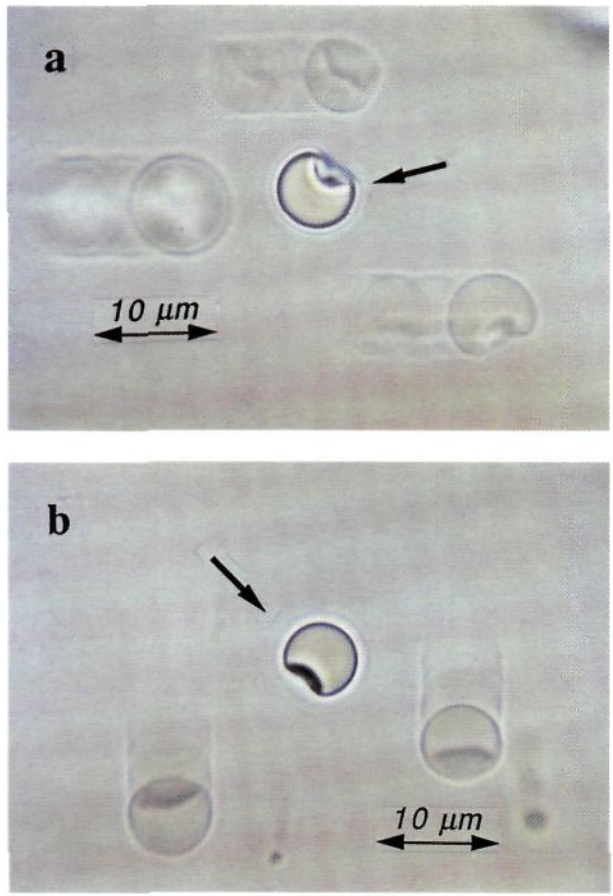

Figure 2. Laser trapping of a pyrene/toluene microcapsule in water along the X (a) or Y (b) direction of the microscope stage. The photographs were taken with the sample stage of the microscope being moved along the X (a) or Y (b) direction. The capsule indicated by the arrow is laser-trapped by 72 mW of the 1064-nm laser beam. See also test.

the inner toluene solution. A laser beam will be refracted at the interface between the surrounding water and the resin as well as between the resin and the toluene solution. For the nonspherical microcapsule such as in Figure 2, in particular, a laser beam will be refracted in a complexed manner. Nonetheless, the microcapsule was easily manipulated three-dimensionally similar to polymer latex particles. The laser trapping force is strong enough for manipulation of an individual microcapsule or a polymer latex particle in water.

For the experiments in Figure 2, the CW Nd^{3+}:YAG laser was operated at 1.25 W. However, the actual laser power illuminated on the capsule under the microscope is reduced to 75 mW (6% of the incident laser beam power) owing to the reflectance of DM1 and the transparency of OL at 1064 nm. Our recent results on trapping of a PMMA particle in ethylene glycol at room temperature indicate that the laser trapping force exerted on the particle is several piconewtons.[10] It is noteworthy, therefore, that the trapping laser beam power as small as several tens milliwatts and the resulted laser-trapping force of the order of piconewtons are sufficiently enough for three-dimensional optical manipulation of a single micrometer-order particle in solution.

Laser Trapping–Spectroscopy of a Single Microcapsule. The chemical nature of individual microparticles randomly dispersed in solution can be characterized/identified by our laser trapping–spectroscopy technique. In the present case, the laser-trapped pyrene/toluene microcapsule (trapping laser power ~ 72 mW) was irradiated by the 355-nm laser pulse (0.39 J/pulse/cm^2).[18] The microcapsule showed efficient pyrene excimer formation as

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(18) Since the laser pulse is focused into a micrometer spot, the actual pulse energy irradiated to the sample solution is 3.9 nJ/pulse/μm^2. For determination of the laser beam energy under the microscope, see ref 10.

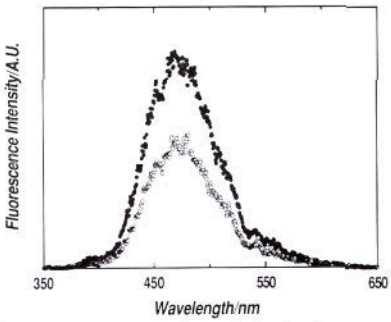

Figure 3. Fluorescence spectra observed for the laser-trapped pyrene/toluene microcapsule ([Py] = 0.1 M, closed circles) and the droplet ejected from the capsule upon ablation (open circles). See also text.

revealed from characteristic fluorescence of monomer and excimer around 370–400 and 475 nm, respectively (Figure 3). Although *the vibrational structure of the monomer fluorescence is not* discernible from Figure 3, close inspection of the spectrum indicates that the fluorescence intensity ratio of excimer (I_E at 475 nm) to monomer (I_M at 385 nm) in the capsule ($I_E/I_M \approx 29$) almost agrees with that in the mother pyrene/toluene solution before preparation of the capsules ($\sim$25). For detailed elucidation of photochemical/photophysical processes occurring in individual microcapsules, the excitation light source and the detector of the laser trapping–spectroscopy system in Figure 1 can be replaced by a picosecond dye laser and single photon counting electronics, respectively.[19] Characteristics of the pyrene excimer formation in the microcapsules have been reported elsewhere.[20]

Laser Trapping–Ablation of a Single Microcapsule in Water. When the laser-trapped microcapsule (Figure 4a, diameter $\sim$10 μm) was irradiated by an intense laser pulse (355 nm, 15 J/pulse/cm^2), deformation of the spherical capsule was observed as clearly seen in Figure 4b. Further increase in pulsed-laser energy led to ablation of the capsule as shown in Figure 4c. The melamine resin capsule wall was decomposed by the one-shot laser pulse (490 J/pulse/cm^2), and pyrene/toluene droplets shown by the arrows in Figure 4c were ejected into the water phase. Upon laser pulse irradiation around 25 J/pulse/cm^2, on the other hand, a small bubble was confirmed to be produced inside of the microcapsule as shown in Figure 5.

As an interesting feature of the trapping–ablation, if an untrapped capsule was irradiated by the laser pulse, the capsule was pushed out from the ocular field of the microscope and we could not confirm laser ablation. Laser trapping is therefore a necessary condition for precise fabrication of individual microcapsules. It is noteworthy, furthermore, that the pyrene/toluene droplets ejected from the ablated capsule were also freely manipulated by the laser-trapping technique. The droplets were characterized by the trapping–spectroscopy technique as the spectrum is included in Figure 3. Although the fluorescence intensity observed for the ejected droplet is different from that for the microcapsule before ablation, this will be explained by the differences in the diameter and the reflection coefficient at 355 nm between the capsule and the droplet. Since I_E/I_M of the two spectra almost agree with each other, the inner solution is ejected from the capsule without any significant decomposition of the components.

The laser pulse energy of 15 or 490 J/pulse/cm^2 necessary for deformation (Figure 4b) or ablation (Figure 4c) of the microcapsule in water, respectively, is extremely high as compared with that for conventional laser ablation of polymer films. For example, the threshold energy for excimer laser (248 nm) ablation of a PMMA film in air is $\sim$500 mJ/pulse/cm^2.[21] In the case of laser ablation of polymer films, furthermore, it has been reported that

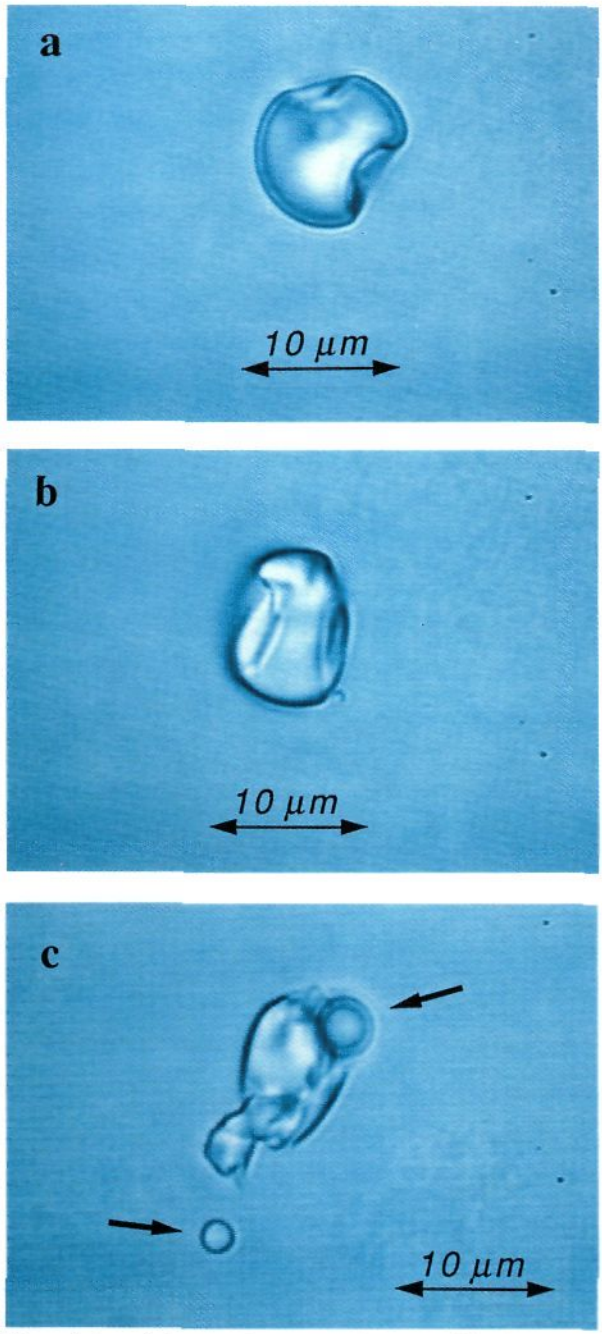

Figure 4. Laser-induced deformation and ablation of the laser-trapped pyrene/toluene microcapsule ([Py] = 1.0×10^{-2} M) in water (laser-trapping energy (1064 nm) 72 mW): (a) before pulse irradiation and (b) laser-induced deformation (pulse energy 15 J/pulse/cm^2) and (c) ablation (pulse energy 490 J/pulse/cm^2) of the microcapsule. The spherical particles indicated by the arrows in Figure 4c are the pyrene/toluene droplets ejected form the capsule upon laser ablation.

the etching rate is strongly dependent on the static pressure of foreign gas.[22] Static pressure being applied to the irradiated part of the capsule by the surrounding water will be one reason for the high threshold of the present ablation. It should be emphasized, however, that the incident laser beam is focused into a $\sim$1-μm spot for trapping–ablation, so that the actual laser pulse energy irradiated to the single microcapsule is as low as nanojoules to microjoules per pulse.

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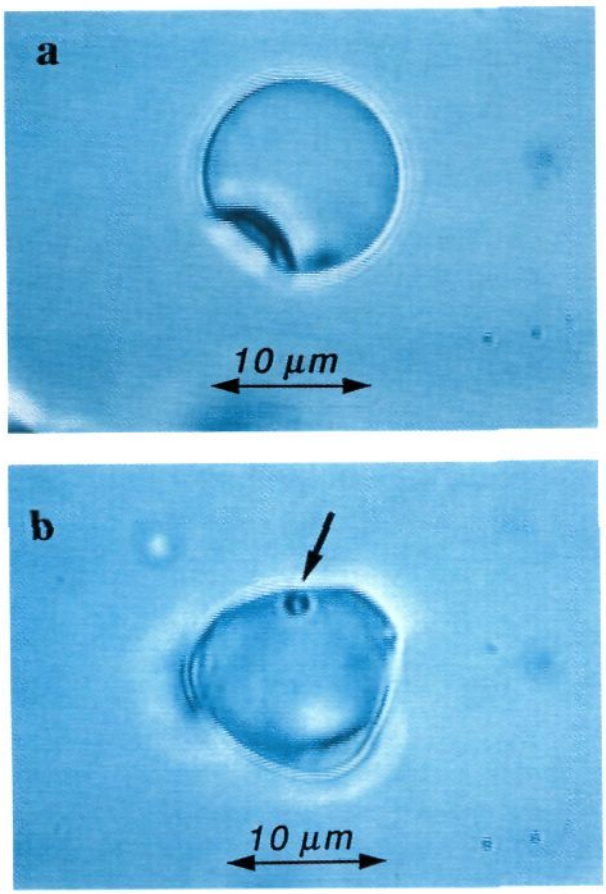


Figure 5. Laser-induced bubble formation in the laser-trapped pyrene/toluene microcapsule ([Py] = 1.0×10^{-2} M) in water (laser trapping energy 72 mW): (a) before laser pulse irradiation, (b) after 355-nm laser pulse irradiation (25 J/pulse/cm^2). The particle indicated by the arrow in (b) is the bubble produced by pulsed-laser irradiation.

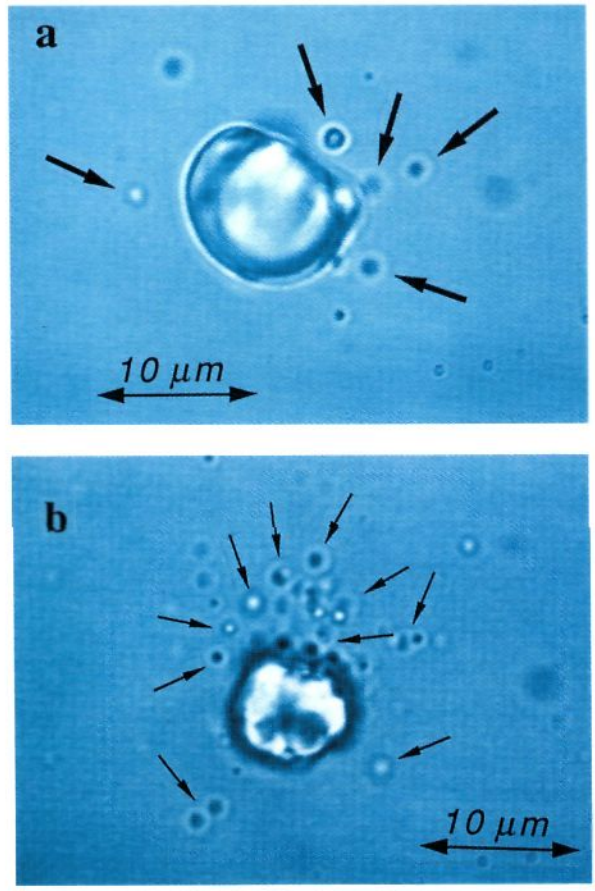


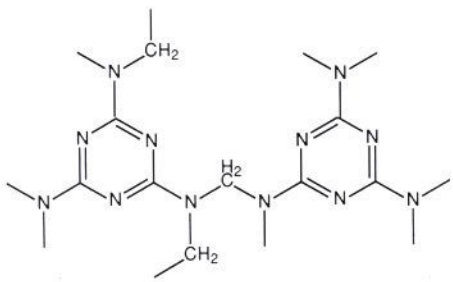
Figure 6. Laser ablation of the laser-trapped pyrene/toluene microcapsule ([Py] = 1.0×10^{-2} M) in water at the pulse energies of (a) 40 and (b) 95 J/pulse/cm^2. The small particles indicated by the arrows are the pyrene/toluene droplets ejected or permeated from the capsule. The small particles in the vicinity of the capsules were also ejected upon pulse irradiation (laser trapping energy 72 mW).

Table I. Pyrene Concentration Dependence of the Threshold Energies for Deformation, Bubble Formation, and Ablation of the Laser-Trapped Microcapsule in Water

	threshold energy,[a] J/pulse/cm^2		
[Py], M^{-1}	deformatn[b]	bubble formatn[b]	ablatn[b]
0	42	42[c]	100
1.0×10^{-2}	7.8	25	40
0.11	5.0	13	13

[a] Threshold energy upon single-shot pulse irradation (355 nm) unless otherwise noted. [b] Typical examples of deformation, bubble formation, and ablation of the capsule are in Figures 4b, 5, and 4c, respectively. [c] Threshold energy upon multishots pulse irradiation (355 nm).

Chart I



In the absence of pyrene in an inner toluene solution of the capsule, the threshold energy for deformation, bubble formation, or ablative decomposition[23] analogous to the result in Figures 4b, 5b, or 4c, respectively, was estimated as summarized in Table I. Since the capsule without pyrene is transparent at 355 nm, ablative photodecomposition of the capsule should proceed via simultaneous multiphoton absorption of the 355-nm laser pulse by the melamine resin capsule wall and/or toluene. Simultaneous multiphoton absorption of a 355- or 266-nm laser pulse has been reported for neat toluene,[24-26] solid polystyrene films,[27] and so forth.[28] The two-photon absorption energy of a 355-nm laser pulse (7.0 eV) is close to the ionization energy of toluene or related compounds (6.3–7.0 eV), so that photoionized species are likely to be produced during simultaneous multiphoton absorption processes of these compounds as proved by picosecond transient absorption spectroscopy.[24-27] The trialkylamino-*s*-triazine structure of the capsule resin (Chart I) is also expected to undergo simultaneous multiphoton absorption of the 355-nm laser pulse similar to toluene and polystyrene. In the absence of pyrene, therefore, multiphoton ionization and subsequent bond scission of the melamine resin wall will be one of the possible origins for ablative decomposition of the microcapsule.

On the other hand, multiphoton absorption by toluene producing ionic species and high excited states does not directly lead to bond scission of the capsule wall, but contributes to ablative decomposition via thermal effects. Namely, recombination of the ionic

(23) In this study, the threshold energy for ablation is defined as the pulsed-laser energy at which ejection of small pyrene/toluene droplets from the microcapsule is observed upon laser irradiation.

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species and/or nonradiative decay of the high excited states will result in local heating and subsequent vaporization of the inner toluene solution. Since local heating/vaporization of toluene accompanies an increase in the vapor pressure inside of the capsule, the melamine resin wall will be decomposed by expansion of the inner volume via such thermal effects. Vaporization of the inner toluene solution upon laser pulse irradiation is experimentally supported by the observation of a small bubble inside of the capsule (Figure 5b).

For the pyrene/toluene microcapsules, pyrene in an inner toluene solution absorbs the 355-nm laser pulse. Therefore, the threshold energy for deformation, bubble formation, or ablation should be dependent on the concentration of pyrene, [Py], in the capsule. Indeed, the ablation threshold was determined to be 40 or 13 J/pulse/cm^2 for the capsule with [Py] = 1.0×10^{-2} or 0.11 M, respectively. Similarly, the pulse energy for deformation or bubble formation of the capsule was dependent on [Py] as summarized in Table I.[29] A decrease in the threshold energy with increasing [Py] in the capsule clearly indicates an important role of pyrene for the results in Figures 4 and 5. Local heating/vaporization of the inner toluene solution will be responsible for deformation, bubble formation, or ablation of the capsule analogous to the results of multiphoton absorption by toluene in the capsule. Local heat generated in the inner solution should be higher for the capsule with higher [Py], so that a decrease in the threshold energy with increasing [Py] is a reasonable consequence as expected from the thermal effects mentioned above. For the capsule with [Py] = 0.11 M, the bubble formation accompanies simultaneous decomposition of the capsule wall as revealed from the same threshold energy for both ablation and bubble formation, 13 J/pulse/cm^2 (Table I). The results support vaporization of toluene upon laser irradiation and subsequent vapor pressure induced decomposition of the capsule.

Another characteristic feature of the present laser ablation is the variation of the ejection mode of the pyrene/toluene droplets with the pulsed-laser energy. Namely, when laser irradiation on the trapped capsule ([Py] = 1.0×10^{-2} M) was performed around the ablation threshold (40 J/pulse/cm^2), small pyrene/toluene droplets were ejected or permeated from the capsule as clearly seen in Figure 6a. An increase in the laser pulse energy (95 J/pulse/cm^2) resulted in ejection of a number of small droplets from the capsule (Figure 6b). Upon pulse irradiation far above the ablation threshold (490 J/pulse/cm^2), on the other hand, ejection of relatively large droplets was observed (Figure 4c). In Figure 6a, the spherical melamine–resin wall of the original capsule can be seen while the capsule wall is completely decomposed to eject the droplets in Figures 4c and 6b. With increasing laser pulse energy, local heat or vapor pressure generated in the capsule increases and, therefore, the number of the ejection or permeation site of the droplet increases as demonstrated in Figure 6. Irradiation of the capsule at 490 J/pulse/cm^2, however, leads to simultaneous decomposition of the capsule wall like *popcorn*, which renders ejection of relatively large droplets (Figure 4c). The results indicate that the ejection or release mode of the inner solution from the microcapsule can be controlled by the laser pulse energy. It has been known, furthermore, that dye sensitization is highly effective for laser ablation of various polymeric materials.[30,31] An appropriate choice of a dye doped into the capsule wall or added to the inner solution will be promising to reduce the ablation threshold as well as to control ablation behavior of the capsule.

Conclusion

The present results clearly demonstrate that the laser trapping–spectroscopy–ablation technique is highly potential to induce and follow chemical reaction in an individual micrometer-order particle in solution. In the present case, indeed, it was shown that a single microcapsule could be easily fabricated by a pulsed-laser beam and ejection of the inner solution from the capsule upon ablation was controlled by the pulsed-laser intensity. Spectroscopic characterization of both the laser-trapped capsule and the droplet ejected upon ablation was also achieved. To the best of our knowledge, simultaneous manipulation, characterization, and fabrication of a single particle cannot be attained except for the use of the present technique. Quite recently, furthermore, we succeeded in spatial alignment of micrometer-order particles in arbitrary patterns produced by interferrence[11] or repetitive scanning[12] of the trapping laser beam(s). In principle, the technique can be extended to align plural microcapsules in any spatial pattern, so that laser trapping–ablation of such spatial patterns of capsules may contribute to laser-printing technology as well. Chemical applications of laser trapping are certainly fruitful in both basic and industrial research, and the works along this line are progress in our project.

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Registry No. Pyrene, 129-00-0; toluene, 108-88-3.

(29) Assuming the diameter of a microcapsule to be 10 μm, absorbance of pyrene in the single capsule at 355 nm is calculated to be 4.7×10^{-3} to $\sim 5.2 \times 10^{-2}$ for the pyrene concentration of 1.0×10^{-2} to ~ 0.11 M ($\epsilon_{355} = 470$ M^{-1} cm^{-1}).

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