Effect of UV−Irradiation on Polyelectrolyte Multilayered Films and Hollow Capsules Prepared by Layer-by-Layer Assembly

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ABSTRACT: Polymer multilayered films were assembled onto planar and particle substrates by the alternate adsorption of oppositely charged polyelectrolytes. Removal of the template from the coated melamine formaldehyde (MF) particles yields hollow polyelectrolyte capsules. The changes in morphology and chemical structure of the capsules after exposure to UV light over a range of intensities and time were characterized by transmission electron microscopy (TEM), Fourier transform infrared (FT-IR) spectroscopy, and quartz crystal microgravimetry (QCM). Pronounced shrinkage of the capsules was observed after UV irradiation for capsules formed with polyelectrolytes bearing aromatic groups, such as poly(sodium 4-styrenesulfonate) (PSS). Capsules composed of five bilayers of PSS and poly(diallyldimethylammonium chloride) (PDDA) shrunk to ca. 20% of their original diameter after UV irradiation (20 mW cm^{-2} at 365 nm) for 120 min. In contrast, negligible shrinkage was observed for capsules formed from polyelectrolytes without aromatic groups (e.g., poly(potassium vinyl sulfate) (PVS)/PDDA). FT-IR spectroscopy reveals that UV irradiation causes chemical changes in the polyelectrolytes with aromatic groups: the disappearance of bands assigned to aromatic groups and the formation of byproducts via chemical changes, such as SO_4^{2-} ions, were observed. In addition, QCM frequency changes showed a decrease in film mass for polyelectrolyte multilayer films formed on planar surfaces that were subjected to UV irradiation, indicating changes in the film properties. UV irradiation causes changes in chemical composition of the capsules, which leads to structural rearrangement and capsule shrinkage. The role of UV irradiation on capsules could be used as a viable route to alter the chemical and physical properties of polyelectrolyte capsules after their formation. This strategy may be potentially useful in environmental applications, where it could be used to modulate the release of substances encapsulated in the capsules upon direct exposure to sunlight, or in UV-initiated chemical reactions in confined microreactor systems.

Introduction

Layer-by-layer (LbL) assembly is widely used as a powerful and versatile method for the preparation of ultrathin multilayered films. This technique, first introduced by Iler in 1966,[1] was developed by Decher and co-workers in 1990s for oppositely charged polyelectrolytes.[2] Such multilayered films can be assembled by alternately dipping substrates into solutions containing oppositely charged polymers. The principal factor for successful deposition of films is the reversal of surface charge upon polyelectrolyte deposition. The preparation of such films has been demonstrated for a range of polyelectrolytes. A variety of charged species, including biomacromolecules (enzymes and proteins),[3,4] lipid bilayers,[5] dye molecules,[6] and inorganic nanoparticles,[7] have been incorporated in LbL assemblies by sequential adsorption with polyelectrolytes. In the late 1990s, LbL assembly was extended to three-dimensional substrates, including colloidal particles.[8,9] Polystyrene latexes,[8] melamine-resin particles,[9] silica particles,[10] biological cells,[11] and organic and inorganic crystals[12] can be used as particle templates (or cores) for depositing the films. Subsequent removal of the cores from these core−shell particles yields hollow microcapsules,[8−13] which are increasingly finding interest as systems for controlled drug delivery applications.

The structure, thickness, and properties of LbL multilayered films are affected by a number of parameters, including polyelectrolyte molecular weight, concentration, and charge density, deposition time, solution ionic strength and pH, and temperature.[14−17] The film properties can also be altered by posttreatment of the films, for example, by varying the temperature,[18−20] exposure to salt-containing solutions,[21] or by changing the solution pH.[22−24] Several studies have focused on the release of guest molecules from LbL multilayered films formed on planar supports. Rubner et al. reported the loading and pH-sensitive release of methylene blue from poly(acrylic acid) (PAA) and poly(allylamine hydrochloride) (PAH) multilayer films.[25] Adsorption-triggered release was reported for pyrene tetrasulfonic acid embedded in LbL multilayer films upon exposure to poly(styrenesulfonate) (PSS).[26] Sukhishvili et al. prepared hydrogen-bonded LbL films of poly(*N*-vinylcaprolactam) and poly(vinyl methyl ester) with poly(methacrylic acid),[19] which could be triggered by temperature changes. The thermoresponsive properties of LbL multilayered films formed with poly(styrene-*alt*-maleic acid) and poly(ethylene oxide) was also demonstrated,[18b] with the films showing a strong affinity for Rhodamine B and releasing the adsorbed dye by elevating the temperature. These earlier studies[18b,19,25,26] are of importance in applications where the release of various substances is required.

In contrast to LbL films formed on planar supports, LbL assembled hollow capsules offer the advantages of enhanced volumes for encapsulating substances and being dispersed (often colloidal) systems. Since these capsules are free-standing they

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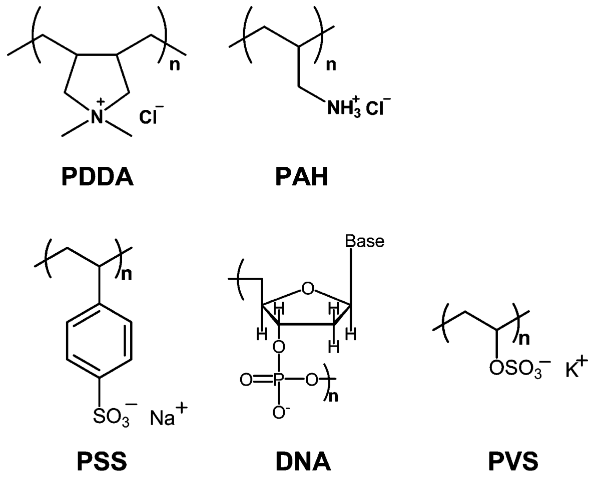
display different properties to their corresponding planar films when subjected to external stimuli.[27] Therefore, studies into the stability and responsiveness of hollow capsules is a critical issue for practical applications such as controlled drug delivery. To this end, recently several studies have been devoted to LbL hollow capsules in an effort to control their permeability properties. The permeability of hollow capsules depends on the pH, ionic strength, solvent, polymer composition, and shell thickness, and this can be controlled and varied using substances with a wide range of molecular weights and charges.[27−35] The sustained release of fluorescent dyes by adjusting the number of poly(allylamine hydrochloride) (PAH)/poly(sodium 4-styrenesulfonate) (PSS) mutilayers has been reported.[28] In addition, it was found that these PAH/PSS hollow capsules are closed or open to high molecular weight polymers depending on the surrounding solution.[29] Advincula and co-workers reported the preparation of hollow capsules formed with LbL assembly of photocross-linkable benzophenone-modifed PAH and PSS.[30] The permeability of dye molecules through the hollow shells was controlled by UV irradiation time, and it was shown that the release of dye molecules can be controlled by the degree of cross-linking induced in the multilayer. The thermal properties of LbL hollow capsules were also investigated and it was shown that incubation of PAH/PSS capsules for 2 h at 70 °C leads to a diameter decrease accompanied by an increase in wall thickness.[31] The same shrinkage effect with increasing temperature was reported for capsules containing thermosensitive polyelectrolytes. Besides the size decrease, a drastic reduction of the permeability coefficient for low-molecular-weight dyes was observed after heat treatment.[32] Studies have also focused on the effects of electromagnetic irradiation on LbL films and capsules.[36,37] We recently showed that gold nanoparticle-functionalized capsules loaded with lysozyme[36b] or FITC−dextran[36c] could be optically addressed by irradiation with near-infrared light to trigger release of the encapsulated substances. However, a detailed study on the influence of UV light on capsules is yet to be reported. This is potentially of relevance in agricultural applications to control the release of encapsulated substances or in modulating chemical reactions within the confined spaces of the capsules.

Herein, we focus on the structural and morphological changes of several types of polyelectrolyte multilayered films and hollow capsules formed by LbL assembly upon UV irradiation. The effects of UV irradiation on the films supported on planar substrates were investigated by quartz crystal microbalance (QCM) and Fourier transform infrared (FT-IR) spectroscopy, respectively. Morphological changes induced by UV irradiation of the hollow capsules were further studied by electron microscopy. We discuss the influence of chemical structure, especially the absence or presence of aromatic rings in the polyelectrolytes (Chart 1), on the response of the films to UV light. These studies provide insight into important chemical, structural, and morphological changes in LbL films upon exposure to UV irradiation.

Experimental Section

Materials. Weakly cross-linked melamine formaldehyde (MF) particles (diameter = 3.05 μm) were purchased from Microparticles GmbH, Germany. Silica particles (diameter = 1 μm) were obtained from Ube-Nitto Kasei Co., Ltd., Japan. Poly(diallyldimethylammonium chloride) (PDDA, M_w 100 000−200 000 g mol^{-1}), poly(allylamine hydrochloride) (PAH, 70 000 g mol^{-1}), poly(sodium 4-styrenesulfonate) (PSS, M_w 70 000 g mol^{-1}), and DNA (sodium salt, from herring testes) were purchased from Sigma-Aldrich. Polyethylenimine (PEI, M_w 1800 g mol^{-1}), poly(potassium vinyl sulfate) (PVS, $(C_2H_3KO_4S = 162.1)_n$, $n > 1500$), hydrochloric acid (HCl) and sodium chloride (NaCl) were obtained from Wako Pure Chemical Industries, Ltd., Japan. All reagents were used as received without any further purification. The water used in all experiments was deionized by an ADVANTEC RFD230NA system (Toyo Seisakusho Kaisha, Ltd., Japan). Quartz crystal microbalance (QCM) resonators (9 MHz, gold electrode, AT-cut quartz) were purchased from USI Co. Ltd., Japan. Gold-coated glass substrates were prepared with a VPC-260 vapor-deposition apparatus (ULVAC, Japan). QCM resonators and gold-coated glass substrates were cleaned via treatment with Piranha solution (70:30 (v/v), sulfuric acid: hydrogen peroxide). ***Caution!*** *Piranha solution is highly corrosive. Extreme care should be taken when handling Piranha solution and only small quantities should be prepared.*

Chart 1



LbL Assembly of Polyelectrolytes on Colloids. The polyelectrolyte multilayer-coated MF particles were prepared by LbL assembly. The positively charged MF particles were suspended in an aqueous solution of an anionic polyelectrolyte (i.e., PSS, PVS, or DNA) (1 mg mL^{-1}) containing 0.5 M NaCl. The anionic polyelectrolyte was allowed to adsorb onto the colloids for 15 min. The dispersion was then centrifuged for 3 min at 2000*g* followed by removal of the supernatant. The polyanion-coated particles were redispersed in deionized water by using a vortex mixer. Before the next coating step, the washing process (centrifugation, removal of supernatant, and redispersion) was repeated twice to remove any nonadsorbed polyelectrolyte. Deposition of a cationic polyelectrolyte (i.e., PDDA or PAH) (1 mg mL^{-1} solution containing 0.5 M NaCl) on the polyanion-coated MF particles was carried out using the same method. The desired number of polyanion/polycation multilayers in the film was obtained by the alternate deposition of anionic and cationic polyelectrolytes onto the particles using this procedure. The deposition process was repeated by using polymer solutions of four different combinations (PDDA/PSS, PAH/PSS, PAH/PVS, and PAH/DNA).

Hollow Capsule Fabrication. Core dissolution of MF was accomplished by exposure of the polyanion/polycation-coated particles (suspended in 0.5 mL water) to 0.1 M HCl solution (1 mL) for 30 min. The hollow capsules were centrifuged and redispersed in pure water. The MF cores were further exposed to HCl several times to remove MF oligomers remaining in the shell and the capsule interior. Finally, the hollow capsules were washed a further three times with pure water.

LbL Assembly of Polyelectrolytes on Planar Substrates. Gold-coated glass substrates and QCM resonators were initially exposed to a PEI solution for 15 min, followed by three 1 min rinses in water to yield positively charged surfaces. The substrates were then exposed to an anionic polyelectrolyte (i.e., PSS, PVS, or DNA) solution for 15 min, followed by three 1 min rinses in water. All polyelectrolyte solutions contained 0.5 M NaCl. Each substrate was then dried under a gentle nitrous gas stream, and the process was repeated, replacing the anionic polyelectrolyte with a cationic polyelectrolyte (i.e., PDDA or PAH). The alternate deposition of polyanions and polycations was performed until five bilayers were adsorbed. The deposition process was repeated for polymer solutions of four different combinations (PDDA/PSS, PAH/PSS, PAH/PVS, and PAH/DNA).

UV Irradiation. UV irradiation of the planar LbL multilayered films and the hollow capsules was carried out with a mercury−xenon lamp (Deep UV lamp) (Spot Cure SP-7, USHIO INC.). For irradiation with a UV cutoff less than 300 nm, the samples were irradiated from the outside through a glass filter (nonalkali silicate glass, NA35, NH Techno Glass, Japan). The hollow capsules were dispersed in deionized water in a cuvette. The cuvette was placed into a cooling bath to avoid heating due to irradiation with the lamp. The dispersions were continuously stirred with a magnetic stirrer during UV irradiation. To reduce temperature increases for the capsule dispersions, the samples, contained in cuvettes, were placed in an ice bath during UV irradiation. Recording the temperature of the dispersions for all experiments showed that increases in the solution temperature was less than 10 °C.

Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) Measurements. The morphology changes of the polyelectrolyte hollow capsules were observed by TEM and SEM. TEM measurements were performed with a Hitachi H-800 microscope operated at 120 kV. TEM samples were prepared by depositing a droplet of the dispersion on a carbon-coated copper grid covered with polyvinylformal film and allowing them to air-dry overnight. SEM images of Au-sputtered samples dried on silicon substrates were obtained with a Hitachi HF-2000 electron microscope at 2.0 kV.

FT-IR Measurements. Infrared spectra of LbL multilayered films on gold-coated glass slides were obtained using an FT-IR spectrometer Magna 560 (Nicolet) equipped with an MCT detector. All data were collected in the reflection−absorption spectral (RAS) mode at a spectral resolution of 4 cm^{-1}. The measurements were performed under a stream of dried air.

Quartz Crystal Microgravimetry (QCM) Measurements. QCM measurements were used for detecting mass changes during the LbL coating process and UV irradiation. QCM frequency changes were recorded by the QCM apparatus (UEQ-400 Easy, USI Co., Ltd., Japan). The frequency changes were taken after deposition of each layer and after UV irradiation for 1, 5, 10, 30, 60, and 120 min. The UV irradiation was fixed at 20 mW cm^{-2} (365 nm). The QCM frequency (ΔF) decreases proportionally with an increase in mass on the QCM surface.[38−40] In our system, the following relationship is obtained between adsorbed mass, M (g), and frequency change, ΔF (Hz) by taking into account the characteristics of the quartz resonator:

$$\Delta F = -1.83 \times 10^8 \times M/A \tag{1}$$

Here A is the cross-sectional area of the quartz microbalance between the QCM electrodes (0.16 ± 0.01 cm^2). All experiments were conducted at 25 °C.

Results and Discussion

The effect of UV irradiation on the morphology of hollow polyelectrolyte capsules was studied for systems composed of five polyanion/polycation bilayers, which were assembled on 3.05 μm diameter sacrificial MF particles. We first examined the influence of UV irradiation time at a fixed intensity on the polyelectrolyte capsules by TEM and SEM. Figures 1 and 2 show TEM and SEM images of the hollow capsules composed of five PDDA/PSS bilayers in aqueous solution before and after UV irradiation (fixed at 20 mW cm^{-2}) for different times ranging from 0 to 120 min. The size of the capsules reflected the original size of the core templates, ca. 3.0 μm, before UV irradiation (Figure 1a). The numerous folds and creases and flattening of the capsules observed are attributed to drying the capsule dispersion on a solid surface.[8,9,13] No holes or traces of rupture were identified in the capsules by TEM or SEM. From the images, it is seen that the capsule size systematically decreases with irradiation time, with the size of the capsules decreasing slightly with irradiation up to 30 min, and shrinking more distinctly after irradiation for 60 and 120 min. Before UV irradiation, the capsules show a more collapsed structure than after irradiation, particularly at longer times (Figure 2). Silica particles were also employed as template cores and HF was used for removal core. No differences were observed in the UV-induced shrinkage of the capsules when using silica particles as templates, compared with the MF particles, for PDDA/PSS capsules.

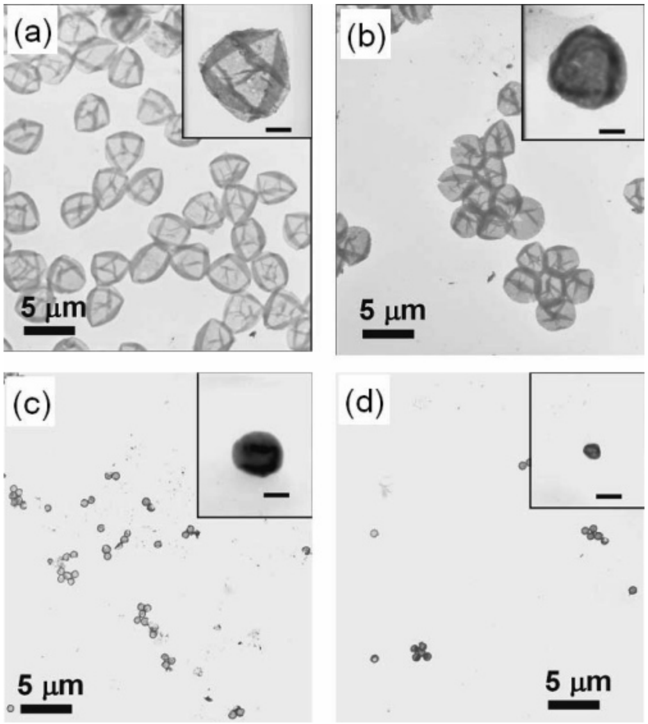


Figure 1. TEM images of (PSS/PDDA)$_5$ polyelectrolyte capsules fabricated with 3.05 μm MF cores before (a) and after UV irradiation for 30 (b), 60 (c), and 120 min (d). The UV irradiation was fixed at 20 mW cm^{-2}. The scale bars for the insets are 1 μm.

The intensity of UV irradiation also influences the capsule size, as depicted in Figure 3 for the 5-bilayer PDDA/PSS capsules. In these experiments, the UV irradiation time was fixed at 30 min. A systematic decrease in capsule diameter was observed with increasing UV irradiation. After UV irradiation at 120 mW cm^{-2} for 30 min, averaging the size of 20 capsules yields a diameter of ca. 1.2 ± 0.1 μm, or about 40% of the original capsule size.

The shrinkage of (PSS/PDDA)$_5$ polyelectrolyte capsules fabricated with 3.05 μm MF cores was quantified by averaging the diameters of at least 20 capsules from the TEM data. The changes in the capsule diameter, expressed as a percentage of the original capsule size, are shown in Figure 4, parts a and b. For the capsules irradiated at 20 mW cm^{-2} as a function of time, the capsule size decreased gradually during irradiation within the first 30 min (size reduction of ca. 20%), followed by a more rapid rate of size change over the next 30 min period, after which the capsule size plateaued at 0.6 μm. The final size represents a total size reduction of about 80% compared with the original capsule diameter. The UV irradiation dependency on intensity (at a fixed time of 30 min) of the capsule diameter is plotted in Figure 4b. In contrast to the data in Figure 4a, after the first 20 min, where a rapid decrease in capsule size is observed, a linear relationship exists between capsule size and irradiation intensity.

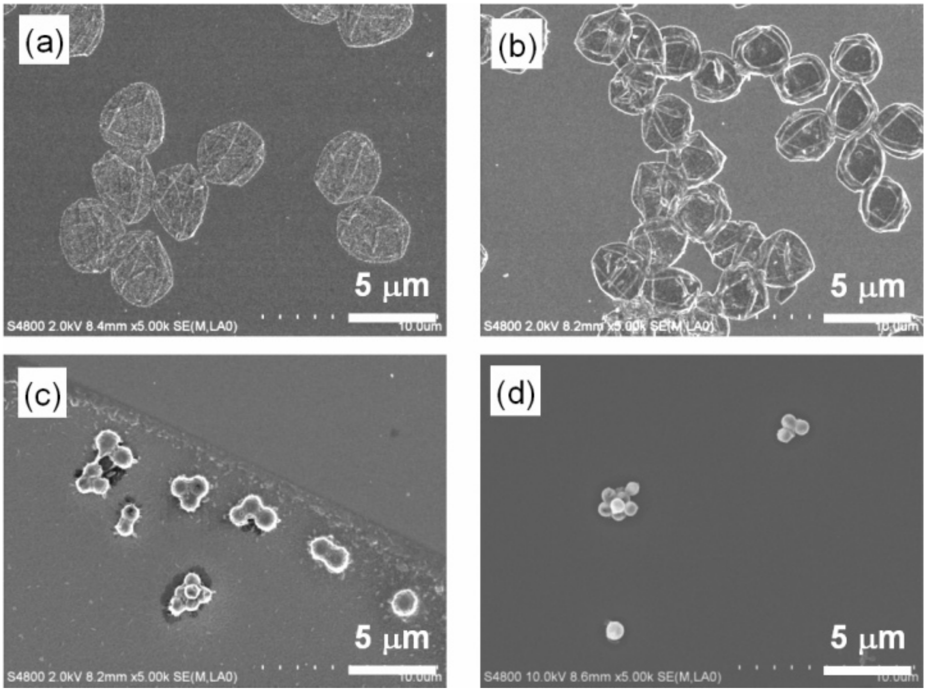


Figure 2. SEM images of (PSS/PDDA)$_5$ polyelectrolyte capsules fabricated with 3.05 μm MF cores before (a) and after UV irradiation for 30 (b), 60 (c), and 120 min (d). The UV irradiation was fixed at 20 mW cm^{-2}.

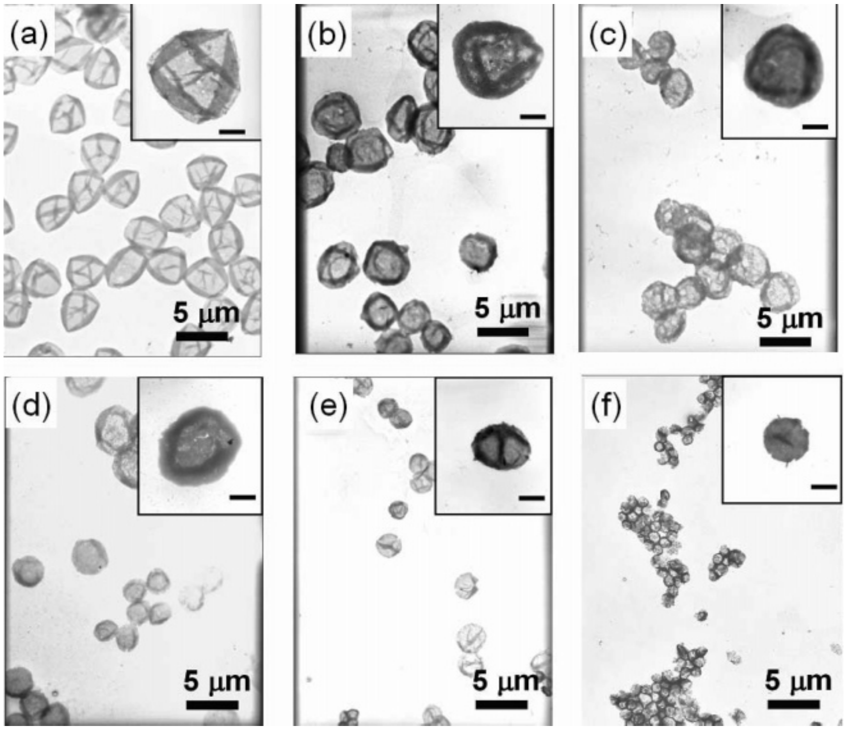


Figure 3. TEM images of (PSS/PDDA)$_5$ polyelectrolyte capsules fabricated with 3.05 μm MF cores after UV irradiation: (a) 0 mW cm^{-2}; (b) 10 mW cm^{-2}; (c) 20 mW cm^{-2}; (d) 40 mW cm^{-2}; (e) 80 mW cm^{-2}; (f) 120 mW cm^{-2}. The UV irradiation time was fixed at 30 min. The scale bars for the insets are 1 μm.

Recently, Köhler and co-workers reported the temperature-dependent behavior of hollow polyelectrolyte capsules consisting of PDDA and PSS in aqueous media.[31d] Capsules with an even number of layers shrunk at elevated temperatures resulting in a transition to dense spheres. However, heating capsules with an odd number of layers resulted in the capsules swelling to five times their initial size and then capsule rupture. This was attributed to an excess of PDDA moieties within the capsules with an odd number of layers, leading to repulsion between the positive charges and swelling. Furthermore, it was reported that capsules with an even number of layers have a balanced ratio between the oppositely charged PDDA and PSS polyelectrolytes. Therefore, the temperature-dependent behavior is influenced by interactions between the polyelectrolytes and the bulk water. In our investigation on the influence of UV irradiation on capsule size, we did not observe any differences in the shrinkage behavior for odd- or even-layer numbered PDDA/PSS capsules (see Supporting Information, Figure S1). This suggests that the UV-induced capsule shrinkage mechanism is different to the process occurring in capsule shrinkage as a result of heat

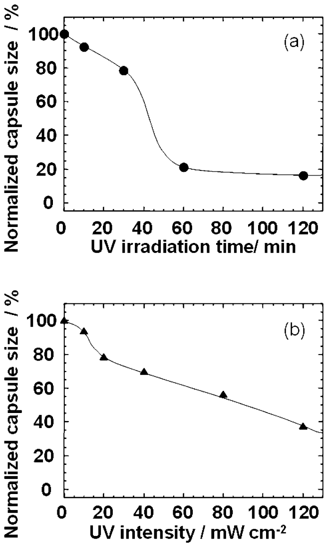


Figure 4. Shrinkage of $(PSS/PDDA)_5$ polyelectrolyte capsules fabricated with 3.05 μm MF cores: relative diameter of capsules as a function of UV irradiation time (20 mW cm^{-2}) (a) and relative diameter of capsules as a function of UV irradiation (with irradiation time of 30 min) (b).

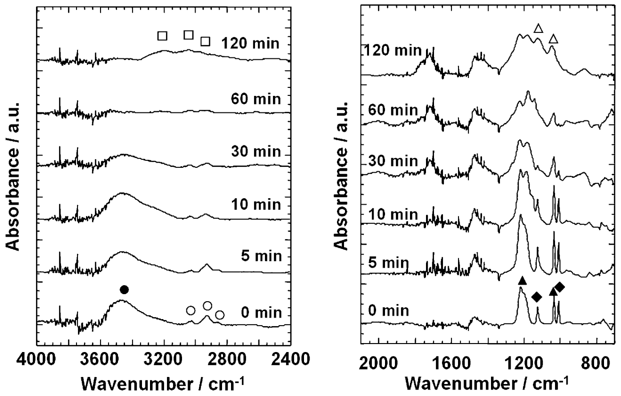


Figure 5. FT-IR/RAS spectra of $PEI/(PSS/PDDA)_5$ multilayered films fabricated on Au-coated glass substrates before and after UV irradiation for 10−120 min. The UV irradiation was fixed at 20 mW cm^{-2}. Closed circles, open circles, closed triangles, open triangles, closed diamonds, and open squares indicate IR peaks for −OH groups, $-CH_3$ and $-CH_2-$ groups, $-SO_3^-$ groups, SO_4^{2-} ions, Ar−H groups, and NH_4^+ ions, respectively.

treatment. This also points away from local heating phenomena as a result of UV irradiation being a significant factor in capsule shrinkage in our systems. However, it is not possible to completely rule out that local heating may play a minor role.

We next used FT-IR/RAS to investigate if UV irradiation caused chemical changes in the PDDA/PSS capsules due to UV irradiation. To probe this, we conducted experiments on PDDA/PSS films prepared on gold-coated planar supports. FT-IR/RAS spectra of five bilayer PSS/PDDA films irradiated at 20 mW cm^{-2} for different times are shown in Figure 5. Prior to UV irradiation, the film exhibited characteristic absorption bands for PSS and PDDA. The relatively sharp bands at 2930 and 2850 cm^{-1} are attributed to the stretching vibrations of the CH_3- and $-CH_2-$ groups, respectively,[41] while the peaks at 1126 and 1009 cm^{-1} are attributed to the bending modes of aromatic rings.[41a] The bands at 1218 and 1034 cm^{-1} and the band at 1198 cm^{-1} are assigned to asymmetric and symmetric vibrations of SO_3^- groups, respectively.[42] Upon exposure to UV light, the intensity of these SO_3^- peaks decreased with increasing irradiation time. After irradiation for 120 min, all original peaks due to the CH_3- and $-CH_2-$ groups, aromatic rings, and SO_3^- peaks reduced in intensity, indicating chemical changes in the polyelectrolytes. We further examined the species that were formed after chemical changes in the polyelectrolytes. After UV exposure, the bands due to the asymmetric and symmetric stretching vibration of $-SO_3^-$ reduced in intensity, and new broad bands appeared at 1130 and 1054 cm^{-1}.[42] These peaks can be assigned to SO_4^{2-}, suggesting that the $-SO_3^-$ group of PSS was converted to SO_4^{2-} during UV irradiation. In addition, the formation of NH_4^+ is indicated by the peaks at 3201, 3047, and 2867 cm^{-1}. These signals can be assigned to the stretching modes of NH_4^+.[42] This indicates that NH_4^+ ions are produced as fragments of PDDA as a result of UV irradiation. The SO_4^{2-} and NH_4^+ formed, as indicated by FT-IR, could act as counterions in the films to maintain charge neutrality. Sasaki et al. also reported the formation of NH_4^+ ions upon UV irradiation for LbL multilayered film containing PSS and PDDA.[43] It is likely that the styrenesulfonate groups and quaternary ammonium groups formed ion complexes in and these complexes were released as salts from the films.

Taking into account the chemical structures of PSS and PDDA, we postulated that the aromatic ring of PSS, which has an absorption band in the UV region (~225 nm; see Supporting Information Figure S2), would be important in inducing the observed morphological changes. Therefore, we prepared capsules with several combinations of polyelectrolytes, both with and without UV absorbing moieties. The differences in the chemical structure of the polyelectrolytes were also investigated. Capsules formed from DNA/PAH and PVS/PAH were used for the comparison experiments. PSS/PAH capsules were used to check the influence of the polycation, DNA was used as a polyanion with UV absorbing properties, and PVS was used as a non-UV absorbing polyanion. The three types of capsules were exposed to UV light with an irradiation intensity of 20 mW cm^{-2} (at 365 nm) for 120 min. TEM observations were carried out for the samples before and after UV irradiation to follow morphological changes of the capsules. Additionally, another set of experiments for the PSS/PDDA capsules were performed with a glass filter that cuts off UV light less than 300 nm. These samples were also investigated by TEM before and after irradiation. Figure 6 shows TEM images of the various hollow capsules before and after UV irradiation. The hollow capsules formed with PSS/PAH shrunk to less than 50% of their original diameter after UV irradiation for 120 min. Use of PSS/PDDA capsules gave a similar result (data not shown), so using a different polycation, whether strong (PSS) or weak (PAH), did not influence the shrinkage behavior with respect to size. The hollow capsules also shrunk drastically after UV irradiation when DNA/PAH was employed for multilayer formation. However, the hollow capsules formed from PVS/PAH showed a negligible reaction, even after UV irradiation for 120 min. DNA has UV absorbing groups, such as adenine, thymine, guanine, and cytosine (the UV−vis spectra of DNA in solution is available in Supporting Information Figure S3) whereas PVS has no UV absorbing moiety. Therefore, these results indicate that the absorbing groups in the polyelectrolytes play an important role in the shrinkage behavior of the hollow capsules exposed to UV irradiation. The result for UV irradiation of PSS/PDDA capsules in the presence of the glass filter (UV cutoff of 300 nm) also supports this argument—the capsules retained almost their original size after irradiation for 120 min. In this case the irradiation was also fixed at 20 mW cm^{-2} at 365 nm but light less than 300 nm was cut off by the filter. In summary,

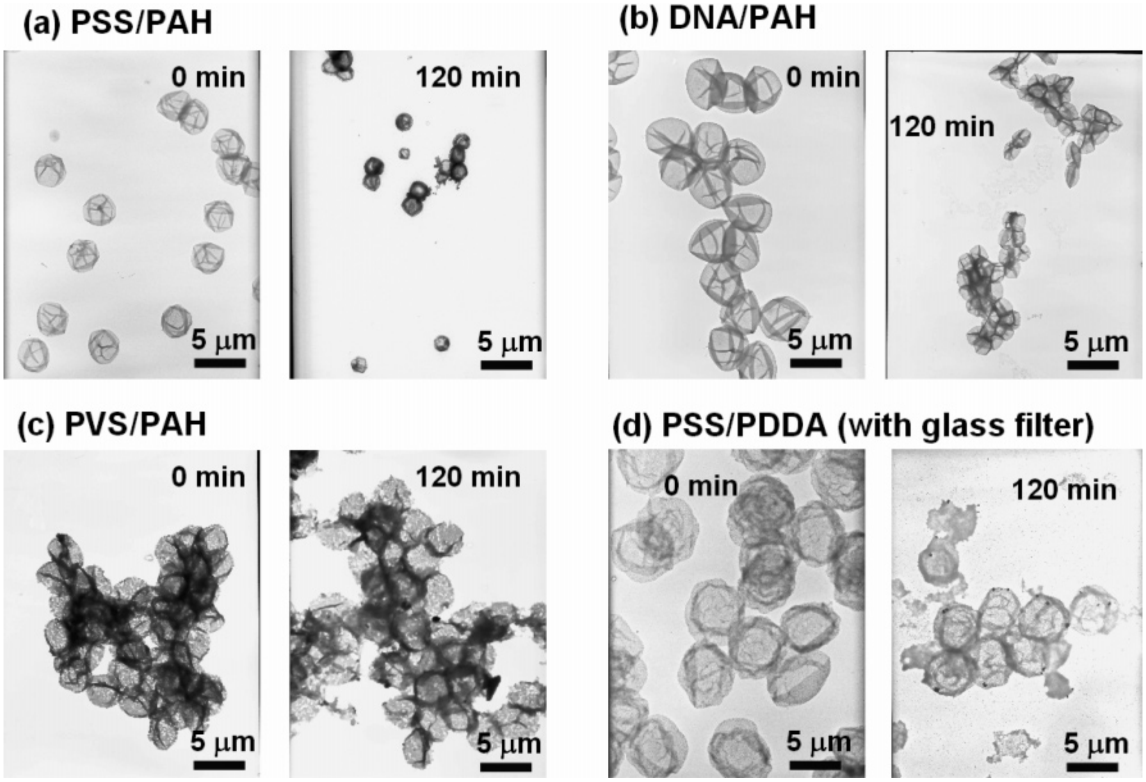


Figure 6. TEM images of hollow capsules formed with several combinations of polyelectrolytes using 3.05 μm MF cores as templates before and after UV irradiation for 120 min: $(PSS/PAH)_5$ capsules (a), $(DNA/PAH)_5$ capsules (b), $(PVS/PAH)_5$ capsules (c), and $(PSS/PDDA)_5$ capsules (d). The UV irradiation was fixed at 20 mW cm^{-2}. In the case of part d, a glass filter that cut off UV light below 300 nm was used.

UV-irradiation causes chemical changes of the polyelectrolytes, which in turn induce morphological changes in the capsules.

To confirm the chemical changes of polyelectrolytes by UV irradiation, QCM measurements were conducted. At first, QCM frequency decreases were measured after deposition of each layer of oppositely charged polyelectrolyte. The combinations of polyelectrolytes, PDDA/PSS, PAH/PSS, PAH/PVS, and PAH/DNA were investigated. Regular film growth was found in all cases by monitoring the frequency of the QCMs. The QCM frequency decreased with increasing polyelectrolyte layer number (see Supporting Information Figures S4−S7). The QCM frequency changes of the multilayers formed from the various combinations of polyelectrolytes upon UV irradiation are shown in Figure 7. All films were composed of five polyanion/polycation bilayers. The UV irradiation of 365 nm was fixed at 20 mW cm^{-2}. For the PSS/PDDA system, the frequency changes upon UV irradiation with a UV cutoff glass filter (<300 nm) were also monitored. For the PSS/PDDA multilayer film, the QCM frequency increased linearly with UV irradiation time, reflecting the proportional weight decrease of the polyelectrolyte multilayer. The weight of the PSS/PDDA multilayer was less than 50% of the original value after irradiation for 120 min (Figure 7a). Similar results were obtained for the PSS/PAH system, where the film weight after UV irradiation for 120 min was ca. 50% of the nonirradiated film (Figure 7c). For the DNA/PAH system, the film weight also decreased with increasing irradiation time and the weight after irradiation for 120 min was ca. 70% of the original film (Figure 7e). This value is relatively high compared to the PSS/PDDA and PSS/PAH systems. DNA molecules sometimes can form thymine dimers under UV irradiation, so the UV light may be used not only for the chemical changes in DNA but also for the formation of thymine dimers.[44] In contrast to the other systems, the frequency increase, i.e., the weight decrease of the PVS/PAH multilayer film upon UV irradiation was quite low—the film retained more than 90% if its original weight, even after irradiation for 120 min (Figure 7d). A similar result was obtained for the PSS/PDDA multilayer film after UV irradiation with a glass cutoff filter (<300 nm); the weight of these films after UV irradiation was more than 80% of the original value (Figure 7b). These results suggest that UV irradiation of the aromatic groups induces changes in the chemical structure of the polyelectrolytes. This causes shrinkage when the multilayers are formed as capsules, as they are not anchored on substrates. It is also noted that even though some mass loss may continue to occur over longer times, the capsules did not change in size.

Conclusions

We have demonstrated the influence of UV irradiation on polyelectrolyte multilayer films fabricated via the layer-by-layer assembly technique. Hollow capsules, obtained by removal of core templates, shrunk drastically after UV irradiation when the capsules were formed from polyelectrolytes with UV absorbing aromatic groups. In a preceding study,[31d] the thermal behavior of the LbL capsules varied depending upon whether an odd or even number of layers was deposited. However, our study found that the capsule response to UV light exposure did not follow this trend, suggesting that UV irradiation of the films proceeds via a different mechanism that induces morphological changes. In part, this is related to the chemical changes of the aromatic groups, i.e., the UV absorbing groups of polyelectrolytes, as confirmed by FT-IR/RAS and QCM measurements. The control experiments—using polyelectrolytes without any UV absorbing groups and using a UV cutoff filter—showed minimal shrinkage of the capsules, even after extended periods of UV irradiation. These results will aid in the selection of polyelectrolytes for the fabrication of multilayered films and capsules that may find application in environmental applications, where the UV-induced

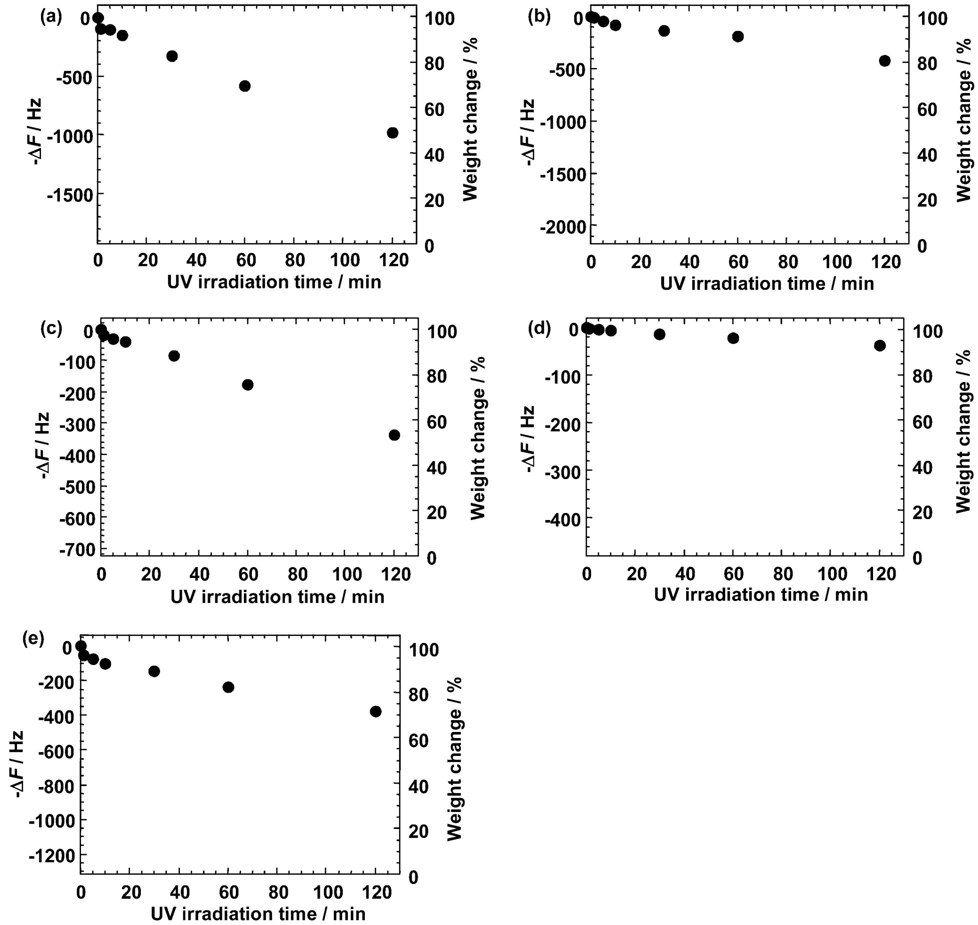


Figure 7. QCM frequency changes of multilayered films formed from several combinations of polyelectrolytes before and after UV irradiation: PEI/(PSS/PDDA)$_5$ film (a, b), PEI/(PSS/PAH)$_5$ film (c), PEI/(PVS/PAH)$_5$ film (d), PEI/(DNA/PAH)$_5$ film (e). The UV irradiation was fixed at 20 mW cm^{-2}. For part b, the UV irradiation was operated with a glass filter that cut off UV light below 300 nm.

shrinkage could be used to modulate the release of substances encapsulated in the capsules upon direct exposure to sunlight, or in UV-triggered chemical reactions in confined polyelectrolyte capsule microreactor systems.

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Supporting Information Available: Figures showing shrinkage of (PSS/PDDA)$_5$/PSS polyelectrolyte capsules (changes in capsule diameters) as a function of UV irradiation time, UV–vis absorption spectra of PSS and DNA in solution with UV irradiation, and QCM data for the multilayer formation of polyelectrolytes as a function of layer number from 0 to 10. This material is available free of charge via the Internet at http://pubs.acs.org.

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