Self-Assembly, Optical Behavior, and Permeability of a Novel Capsule Based on an Azo Dye and Polyelectrolytes

Xia Tao,*[a, b] Junbai Li,*[c] and Helmuth Möhwald[a]

Abstract: A novel capsule composed of an azo dye, Congo red (CR), and different polymers, including poly(styrenesulfonate, sodium salt) (PSS), poly(allylamine hydrochloride) (PAH), and poly(diallyldimethylammonium chloride) (PDDA), have been successfully fabricated by the layer-by-layer self-assembly technique. The stepwise linear deposition process was monitored by means of UV-visible absorption measurements. The formation of hollow capsules was verified by confocal laser scanning microscopy (CLSM) and scanning force microscopy (SFM). The resulting hollow PSS/PAH/CR/PDDA capsules displayed a sensitive response to visible light. Optical changes of the hollow capsules prior to and after the photoreaction were investigated in detail by means of UV-visible spectroscopy, CLSM, and SFM. It was found that the photochemical reaction of the assembled hollow capsules depends strongly on the matrix. Qualitative results on the permeability of the hollow capsule walls with CR as one component indicate that the permeability of the walls can be easily photo-controlled at varying irradiation time intervals without addition of external chemicals.

Keywords: dyes/pigments · fluorescence · hollow capsules · permeability · self-assembly

Introduction

Efficient encapsulation of active ingredients such as living cells, enzymes, drugs, heterogeneous catalysts, and nanoparticles with unique optical, electronic, or magnetic properties is becoming increasingly important for a large variety of applications ranging from drug delivery to biomedicine and materials science.[1,2] Hollow capsules with well-defined internal volume in submicrometer regions are potentially applicable as protective containers for the demanding requirements of these applications.[3] The most attractive method for the fabrication of hollow capsules is the layer-by-layer (LbL) assembly[4], which is simply performed by repetitive alternate adsorption of colloidal templates in aqueous solutions and subsequent removal of colloidal particles. It has been demonstrated that hollow capsule walls can be fabricated by using many functional materials such as biopolymers, inorganic silica, and inorganic/organic composites by means of the LbL assembly technique.[5] The few examples reported to date have shown that water-soluble dyes with low molecular weight can be assembled on the capsule walls. Actually, the incorporation of dye molecules into the coating renders the capsule walls sensitive to external stimuli such as light irradiation;[3c] this results in photoresponsive capsules, for example, as light-harvesting antenna for solar energy conversion, photocatalysis, optical materials, and skin care or plant protection.

Many efforts have been devoted to the development of more simple and reliable methods to better control the permeability of the hollow capsule walls.[6] Although a variety of release strategies for the controlled permeability of the hollow capsule walls may be feasible, either through control of the pH value, temperature, and salt concentration, or through the control of an enzymatic cleavage reaction,[7–9] for many applications it is highly desirable to control the permeability by photoirradiation. This requires building the capsule walls with dyes as one component and controlling their photoreactions and consequences.

In recent years, azo dye-containing polymers with large photoinduced birefringence and high thermal stability have been extensively investigated in view of the increasing demand for large-scale information storage.[10] Congo red (CR), an azo dye with two negative charges and a chromo-

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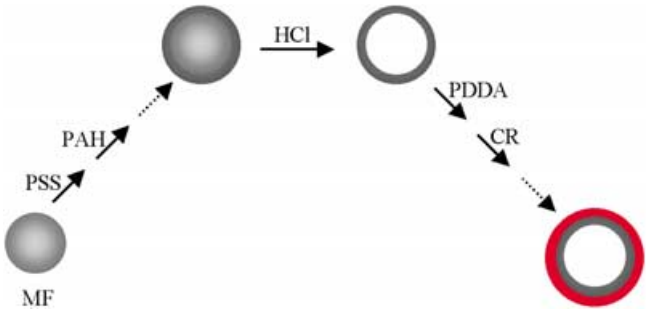
phore moiety, has been incorporated into polymer films by means of the electrostatic LbL deposition technique.[11,12] It has been demonstrated that dyes can be moved by visible light irradiation over micrometer distances in CR/PDDA (PDDA = poly(diallyldimethylammonium chloride)) films.[13] We consider in this paper the construction of three-dimensional multilayered capsules by using CR and PDDA as building blocks, and investigating the optical behavior and permeability of the assembled hollow capsules upon illumination with visible light.

The preparation of hollow capsules of CR/PDDA by the alternate electrostatic deposition of the respective charged species (CR or PDDA) onto the $(PSS/PAH)_3/PSS$ (PSS = poly(styrenesulfonate, sodium salt); PAH = poly(allylamine hydrochloride)) shells templated on melamine formaldehyde (MF) is reported. The formation of (PSS/PAH/CR/PDDA) hollow capsules was verified by confocal laser scanning microscopy (CLSM), scanning force microscopy (SFM), and UV-visible spectroscopy. The optical behavior of the hollow capsules constructed through electrostatic self-assembly procedures prior to and after the photoreaction were investigated by means of UV-visible spectroscopy, CLSM, and SFM. The permeability of the capsule walls triggered by photoirradiation was investigated by CLSM studies on different fluorescently labeled compounds. Preliminary results demonstrate that the permeability of the capsule walls can be controlled only through exposure to visible light. This study represents a new approach for controlled release by the combination of dye molecules, self-assembly, and light.

Results and Discussion

Fabrication of hollow capsules: Scheme 1 shows the general procedure of LbL self-assembly of PDDA/CR onto the $(PSS/PAH)_3/PSS$ shells templated on MF latex particles. It is well known that CR is an acid/base indicator with a color change from blue to red in the approximate pH range from 3 to 5.[13a,14] In order to avoid the effect of hydrochloric acid (0.1 M) on CR in the course of the removal of the cores, it is essential to remove the colloidal template MF prior to adsorption of CR. Further details of this procedure can be found in the Experimental Section.



Scheme 1. General procedures for the fabrication of hollow capsules composed of CR and polyelectrolytes.

CLSM images provide strong evidence that the composite hollow capsules of $(PSS/PAH)_3/PSS/(PDDA/CR)_n$ or $(PSS/PAH)_3/PSS/(PDDA/CR)_n/PDDA$, (repeating number, $n = 1$, 2, 3, 4, 5) were successfully fabricated by the LbL self-assembly technique. A typical CLSM image as a representative for all fabricated capsules is shown in Figure 1. It can be seen that the fabricated hollow capsules possess an intact spherical architecture, and the strong red fluorescence of CR from the whole capsule surface indicates that the dye has been successfully incorporated into the shells. All fabricated capsules remain stable during a period of at least two months. In addition, we carried out another experiment, according to the same above-mentioned procedure, on the fabrication of the hollow capsule composed of Orange II (4-(2-hydroxy-1-naphthylazo)benzenesulfonic acid sodium salt) with a sulfonato group on the phenyl ring and the same polyelectrolytes as employed above. It was found that almost all the capsules were destroyed upon adsorption of Orange II onto the $(PSS/PAH)_3/PSS$ shells. In view of the structures of these two kinds of azo dyes, it can be concluded that azo dyes with symmetrically charged structures are able to form highly stable capsules. Furthermore, we recently found that phthalocyanine dyes with symmetrically charged structures can also be embedded in the hollow capsule walls and, hence, create stable capsules (details of these procedures and results will be reported elsewhere).

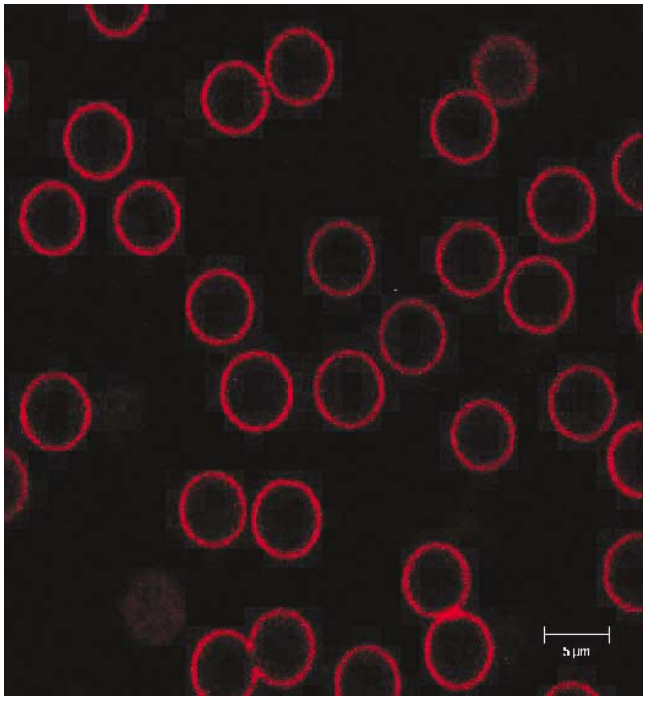


Figure 1. CLSM images of $(PSS/PAH)_3/PSS/(PDDA/CR)_3/PDDA$ capsules templated on MF particles of 5.06 µm. The white bar represents 5 µm.

Figure 2 shows UV-visible spectra of CR in the (PDDA/CR) capsule solution (solid line) and in aqueous solution with 10 mM phosphate buffer (dotted line). Compared with the absorption band in aqueous solution, the maximum absorption peak of the alternate assembly (PDDA/CR) is red-

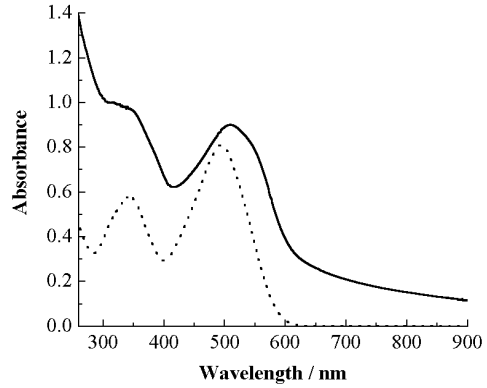


Figure 2. UV-visible spectra of CR in the $(PSS/PAH)_3/PSS/(PDDA/CR)$ capsule solution (solid line) and the aqueous solution of 10 mM phosphate buffer of pH 7.4 (dotted line).

shifted and slightly broadened. This indicates that there are strong electrostatic interactions between the negatively charged CR and the positively charged PDDA. A similar shift has been previously reported in (PDDA/CR) multilayer films, and is attributed to the formation of J aggregates.[11,15] Evidently, binding of CR to the charged polyelectrolyte surfaces of the hollow capsules results in the formation of J aggregates.

The sequential deposition process was easily monitored by UV-visible spectroscopy. The pronounced characteristic absorbance of CR (bright red capsule solutions) provides an additional insight into the layer growth and the degree of CR incorporation. Figure 3 (top) shows absorption spectra for multilayer assemblies with different adsorption cycles. The lowest solid line in Figure 3 corresponds to $(PSS/PAH)_3/PSS$ capsules templated on MF particles of approximately 5 μm; these were used as precursor shells for all PDAC/CR multilayer assemblies. As shown at the bottom of Figure 3, the maximum absorption peaks of CR at 345 nm and 509 nm, corresponding to a $\pi \rightarrow \pi^*$ transition[15], are observed to increase almost in proportion with the number of dye layers (i.e., capsule wall thickness). The linear growth of the characteristic absorption peaks with increasing number of assemblies indicates that the deposition process is highly reproducible and controllable.

The wall thickness of hollow capsules was measured by means of SFM. Figure 4 shows an image of a $(PSS/PAH)_3/PSS/(PDDA/CR)_3$-layer capsule. A number of folds and creases were observed as a result of air-drying. The wall thickness can be deduced from the smallest height of the air-dried hollow capsule. This value corresponds to a double wall thickness. A typical height profile (as indicated by the line in the top view) is given at the bottom of Figure 4. The wall thickness of a $(PSS/PAH)_3/PSS/(PDDA/CR)_3$ layer in the dried state was obtained as 30 ± 4 nm. According to the literature,[16] the thickness of a layer of PAH or PSS is about 1.5 nm. By subtracting the thickness of the $(PSS/PAH)_3/PSS$ layer, the thickness of one (PDDA/CR) bilayer is approximately 65 ± 5 Å, which is in good agreement with the average thickness of one (PDDA/CR) bilayer (65 Å in the composite films).[13a] If the thickness of PDDA is considered to be analogous to that of PAH or PSS, the thickness of a CR

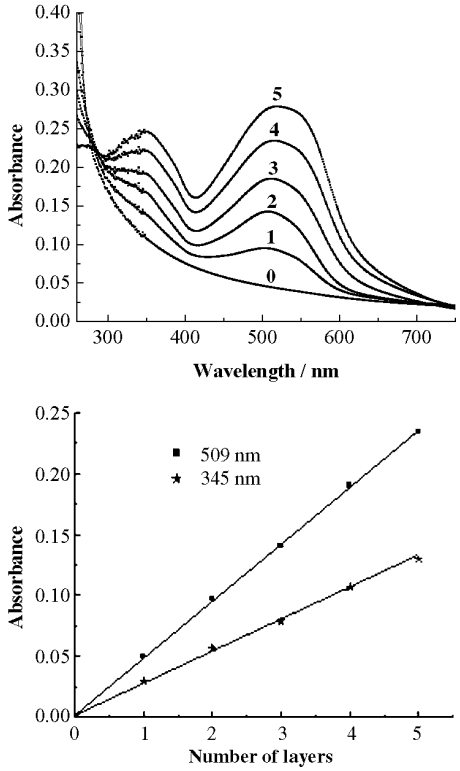


Figure 3. Top: UV-visible absorption spectra of $(PDDA/CR)_n$ ($n = 1, 2, 3, 4, 5$) of alternate assemblies on hollow capsules of $(PSS/PAH)_3/PSS$ obtained by removal of the 5.06 μm MF cores with 0.1 M HCl. The resulting capsules were dispersed in Millipore water at the given volume for measurements. Bottom: The linear growth of CR absorbance at 345 nm and 509 nm with the number of bilayers.

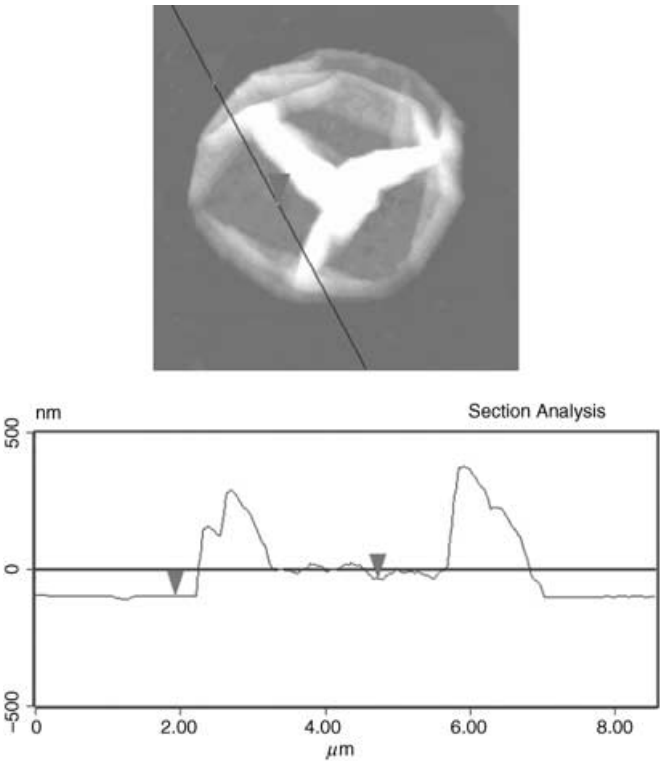


Figure 4. Top: SFM topview image of a $(PSS/PAH)_3/PSS/(PDDA/CR)_3$-layer capsule prepared on the MF resin latex of 5.06 μm diameter. Bottom: section analysis of SFM view along the line as indicated in the top view.

layer is approximately 50 Å. This value is far greater than the lengths of the long axis (19 Å) and short axis (5 Å) of CR[11], and also supports the interpretation of formation of CR aggregates in the composite capsules.

Optical behavior of hollow capsules: The temporal fluorescence intensity changes of hollow capsules composed of $(PSS/PAH)_3/PSS/(PDDA/CR)_3/PDDA$ templated on MF particles under visible light irradiation are displayed in Figure 5. The red rings along the perimeter of the whole

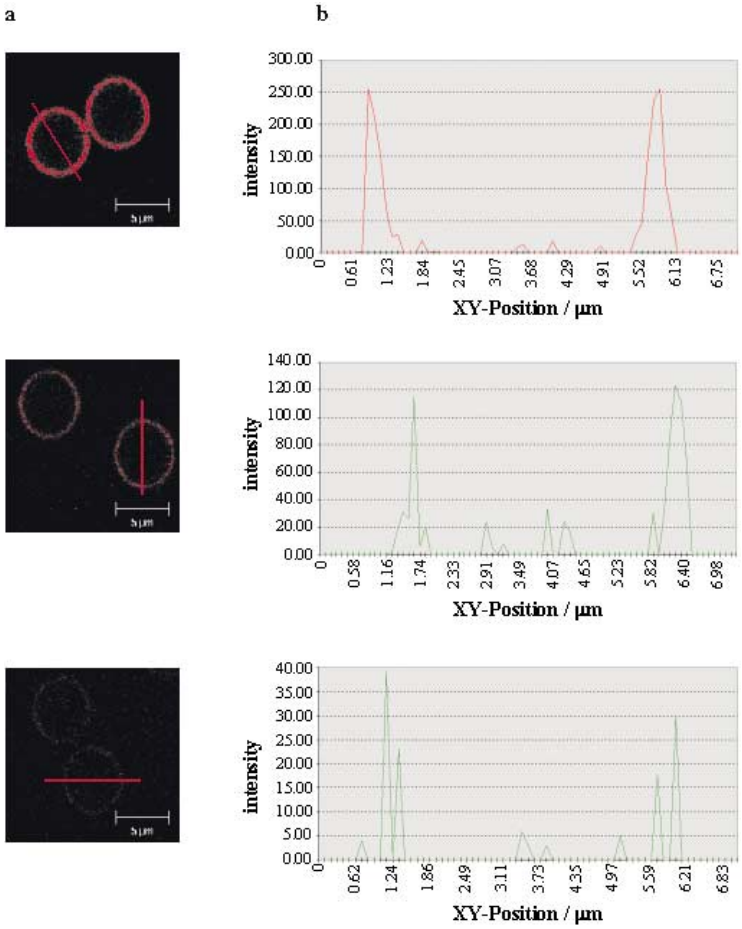


Figure 5. a) Variations in CLSM fluorescence images of hollow capsules of $(PSS/PAH)_3/PSS/(PDDA/CR)_3/PDDA$ with different irradiation time; irradiation from top to bottom: 0, 60, and 120 min. The white bars represent 5 µm. b) Fluorescence profiles of hollow capsules of $(PSS/PAH)_3/PSS/(PDDA/CR)_3/PDDA$ along the line through the capsule center as indicated in fluorescence images.

capsule surface exhibit the fluorescence intensity of CR. As can be seen from Figure 5a, under irradiation, the fluorescence intensity of CR decreases rapidly and almost disappears after irradiation for 120 min; concomitantly, the color of the capsule solution changes from the initial red to yellowish, indicating that at least the chromophoric structure of the CR dye is destroyed. In order to quantify the changes of the fluorescence intensity from the capsule wall, a line has been drawn to cross the capsule center. Figure 5b displays the fluorescence distribution changes along the line at varying irradiation time. Before irradiation, the initial fluorescence intensity (red profile line) is 250 units. After irradiation for 60 and 120 min, the fluorescence intensity (green profile lines) decreases to approximately 120 and 40 units, respectively. It is worth noting that during the whole photoreaction the fluorescence of CR is mainly concentrated on the shells, indicating that the dye molecules are well embedded in the coating. Furthermore, the assembled hollow capsules, even if under illumination with visible light, keep their spherical shape.

The temporal absorption spectra changes taking place during the photoreaction of composite hollow capsules of $(PSS/PAH)_3/PSS/(PDDA/CR)_4/PDDA$ under visible light irradiation are displayed in Figure 6. The characteristic ab-

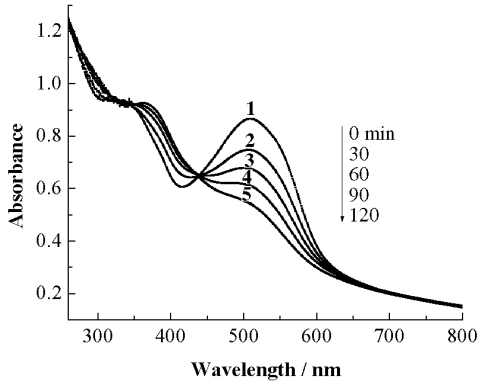


Figure 6. Changes of absorption spectra of hollow capsules of $(PSS/PAH)_3/PSS/(PDDA/CR)_4/PDDA$ under irradiation with visible light. Spectra 1, 2, 3, 4, and 5 denote irradiation for 0, 30, 60, 90, and 120 min, respectively.

sorption band of CR at about 509 nm decreases at a fast rate, and nearly disappears after irradiation for 120 min. Besides, the existence of an isobestic point at 438 nm during the photoreaction indicates a transition between two states, namely from the initial assembled CR to the formed product. A control experiment shows that no changes of the CR UV-visible spectra are observed in aqueous solution. This proves that the photobleaching process depends strongly on the environment. In addition, we measured the absorption spectra changes of the $(PSS/PAH)_3/PSS/(PDDA/CR)_4/PDDA$ capsule solution under otherwise identical experimental conditions as for Figure 6 except under a nitrogen atmosphere. Almost the same photobleaching rate of CR was observed as for that measured under aerated conditions. This implies that in the present system the effect of oxygen on the photoreaction is minor, and also further confirms that the effect of the microenvironment of the capsule wall is predominant.

To gain further insight into the nano- and microcapsule wall texture changes before and after the photoreaction, the SFM technique can be employed.[17] Figure 7a and b display SFM images (topview) of hollow capsules with $(PSS/PAH)_3/PSS/(PDDA/CR)_3/PDDA$ before and after exposure to visible light for 60 min. A number of folds and creases arising from evaporation of the aqueous content were observed.

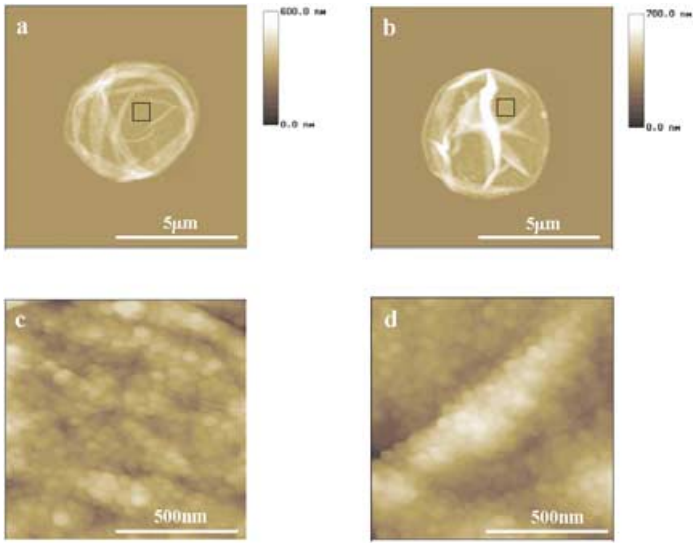


Figure 7. SFM images of air-dried hollow capsules of $(PSS/PAH)_3/PSS/(PDDA/CR)_3/PDDA$ before (a, c) and after (b, d) irradiation for 60 min.

High-resolution SFM observations allow us to inspect the capsule wall surface on the nanometer scale. Capsule wall textures from selected areas in the center of panels a and b of Figure 7 without folds are displayed in Figure 7c and d. An evident difference in the capsule wall before and after the photoreaction was observed, that is, the surface morphology of the latter is rougher than that of the former. Roughness calculations over a 1.0×1.0 μm area free of folds provided roughness values of $\sim 6 \pm 0.5$ nm and 9 ± 0.5 nm before and after the photoreaction, respectively.

Permeability of hollow capsules: The permeability of the hollow capsule walls was investigated by means of CLSM studies on fluorescent-labeled poly-L-lysine and dextran with different macromolecular weights, as well as on the small dye molecule 6-carboxyfluorescein (6-CF). Figure 8

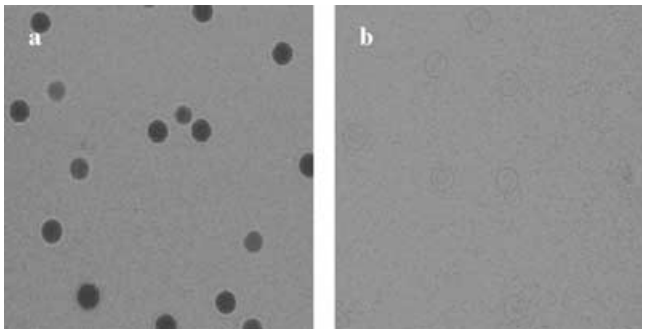


Figure 8. Typical CLSM images of hollow capsules of $(PSS/PAH)_3/PSS/(PDDA/CR)_3/PDDA$ incubated with a fluorescent probe: a) impermeable; b) permeable.

displays typical CLSM images of hollow capsules, considered as impermeable and permeable, measured three minutes after the addition of the labels. More than 30 capsules were counted for one data point. Qualitative permeability variations of hollow capsules of $(PSS/PAH)_3/PSS/(PDDA/CR)_3/PDDA$ before and after illumination with visible light for 60 and 120 min are shown in Table 1. In all cases, the hollow capsules were highly permeable to 6-CF, but completely impermeable to poly-L-lysine and dextran 2 000 000. Before irradiation, the capsule walls were impermeable if dextran with $M_w \geq 4400$ was applied. After 60 min of irradiation, however, dextran 4400 and 66 100 could cross the layer barrier. Further irradiation, namely 120 min of light irradiation, made the capsule walls permeable to dextran 77 000 and 464 000. These results indicate that the permeability of the capsule walls evidently can be photocontrolled simply by exposure to visible light. It is important to note that the photocontrolled release covers the broad range of molecular weights from 4–400 KDa, which includes most proteins. Hence, this yields new potential for applications in pharmacy, medicine, and biotechnology. Further experiments on how to quantitatively control the permeability of the hollow capsule walls under varying light irradiation conditions are under way.

Table 1. Qualitative permeability variation of hollow capsules of $(PSS/PAH)_3/PSS/(PDDA/CR)_3/PDDA$ before and after illumination with visible light for 60 and 120 min, respectively. Note: "0" in the table denotes impermeable and "100" denotes permeable; see text for details.

	No irradiation	Irradiation for 60 min	Irridiation for 120 min
poly-L-lysine	0	0	0
dextran 2 000 000	0	0	0
dextran 464 000	0	0	100
dextran 77 000	0	0	100
dextran 66 100	0	100	100
dextran 4 400	0	100	100
6-CF	100	100	100

Based on all the above experimental results we find that CR in the present hollow capsule system is more likely to exist in the form of aggregates; this is supported by the 15 nm red shift of the maximum absorption peak of CR relative to that of CR in the aqueous solution, and from the thickness of the CR layer (ca. 50 Å), which is greater than the length of the CR axes itself. Upon illumination with visible light, dye aggregates are subject to destruction. Also, we find that the optical changes of the assembled hollow capsules are closely related to the matrix microenvironment. Although for the moment we cannot yet comment on whether pores have been created, a similar surface-morphology change has been observed by assembling mixtures of phospholipids onto the surface of the capsules and inducing release by an enzymatic cleavage reaction.[8a]

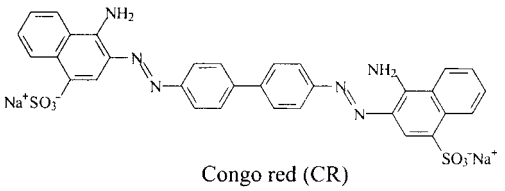
Conclusion

A CR dye can be successfully incorporated into polyelectrolyte hollow capsules by means of the LbL self-assembly technique. The introduction of CR lends the hollow capsule walls new features, for example, the permeability of the shells can be photocontrolled by irradiation with visible

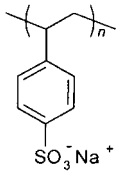
light. The optical changes of the hollow capsules were investigated by UV-visible spectroscopy, CLSM, and SFM. All results obtained provide useful insights into the photochemical reaction mechanisms on the self-assembled PDDA/CR composite hollow capsules. This kind of novel capsule with photocontrolled permeability is of particular interest for applications in drug delivery, photocatalysis, optical materials, and related medical areas such as photodynamic therapy or skin care.

Experimental Section

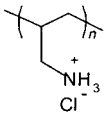
Materials: PSS ($M_w = 70000$), PAH ($M_w = 70000$), and PDDA (20 wt % in water, $M_w = 200000$–350000) were purchased from Aldrich and used as received. CR was obtained from Sigma. MF particles (5.06 ± 0.12 μm) were obtained from Microparticles GmbH, Germany. Fluorescently labeled poly-L-lysine, FITC-labeled dextrans (2000000, 464000, 77000, 66100, and 4400) and 6-carboxyfluorescein (6-CF) were purchased from Sigma and used without further purification. A solution of CR with a concentration of 2.5×10^{-4} M in 0.01 M phosphate buffer solution of pH 7.4 was prepared as the anionic solution, and a PDDA solution with a concentration of 1 mg mL^{-1} in 0.01 M citric acid/sodium citrate buffer solution of pH 4.4 containing 0.5 M NaCl was used as the cationic solution. Solutions of PSS (1 mg mL^{-1}) and PAH (1 mg mL^{-1}) in 0.5 M NaCl were prepared for all experiments. Millipore water was used throughout the study. For reference, the structures of CR, PSS, PAH, and PDDA are shown below.



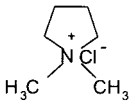
Congo red (CR)



PSS



PAH



PDDA

Procedures for the fabrication of hollow capsules: PSS and PAH were assembled onto the surface of MF microparticles by layer-by-layer adsorption according to the method reported[3,18]. Briefly, a solution (1.5 mL) of PSS or PAH with a charge opposite to that of the MF templates or the last layer deposited was added to a template latex solution (0.3 mL), and left to adsorb for 10 min. The excess added species was removed by three repeated centrifugation (2500 *g*, 2 min)/washing/redispersion cycles with dilute aqueous NaCl. After completion of $(PSS/PAH)_3/PSS$ deposition, hollow capsules were obtained by dissolving the MF core with HCl solution (0.1 M). The resulting hollow capsules were then centrifuged at 2500 *g* for 5 min and washed three times with water. Subsequent alternate adsorption of PDDA and CR was carried out by using a similar procedure, except that the adsorption of CR was left for 30 min. All adsorption procedures were carried out at ambient temperature.

Photoreactor and light source: Unless otherwise noted, all irradiation experiments were carried out in a quartz cell with an appropriate stirrer. A 150 W super-quiet xenon lamp (Hamamatsu, Japan) was positioned inside the E7536 lamp housing with an automatic cooling fan (Hamamatsu, Japan). One side of the lamp housing has a window with an area of approximately 3×3 cm^2. A cutoff filter was placed on the small window to completely remove wavelengths less than 400 nm and to ensure irradiation only by visible light. The center-to-center distance between the reaction vessel and the light source was 6 cm.

Characterization methods: Confocal micrographs were taken with a confocal laser scanning microscope "Aristoplan" from Leica (Germany) equipped with a 100× oil immersion lens. The optical parameters of the CLSM remained unchanged before and after the photoreaction to ensure that the measured intensities could be compared quantitatively.

The absorption spectra of the hollow capsules were measured in Millipore water on a Varian Cary 4E UV-visible spectrophotometer.

The scanning force microscopy (SFM) images were recorded by using a Digital Instruments Nanoscope IIIa in the tapping mode. Samples were prepared by applying a drop of the capsule solution onto a freshly cleaved mica substrate. After the capsules were allowed to settle, the substrate was extensively rinsed in Millipore water and then dried under a gentle stream of nitrogen.

Acknowledgement

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