Highly Stable and Biocompatible Nafion-Based Capsules with Controlled Permeability for Low-Molecular-Weight Species

Zhifei Dai* and Helmuth Möhwald[a]

Abstract: Biocompatible hollow capsules have been formed by electrostatic layer-by-layer self-assembly of a perfluorinated ionomer (Nafion) in alternation with ferric ions onto polystyrene latex particles or organic microcrystals, followed by dissolution of the cores by tetrahydrofuran or dimethylformamide. The stepwise growth of multilayers was followed by UV-visible spectroscopy and microelectrophoresis. The formation of hollow capsules was verified by confocal laser scanning microscopy and scanning force microscopy. The hollow Fe^{3+}/Nafion capsules displayed high stability over a wide range of pH values and at high temperature. Fluorescein transport through the Fe^{3+}/Nafion capsule wall was studied by means of photochemical bleaching and recovery (PBR) of the capsule interior. A diffusion model is suggested to calculate the diffusion coefficient for low-molecular-weight species, which was determined to be in the order of 10^{-12} cm^{2}s. The permeability can be manipulated by changing the wall thickness of the capsules.

Keywords: hollow capsules · Nafion · nanostructures · permeability · self-assembly

Introduction

Encapsulation technologies have developed to reduce toxicity, to mask taste and odor, to facilitate storage or transport, and to improve the stability of the encapsulated product.[1] Hollow polymer particles with dimensions in the submicrometer region possess great potential for encapsulation of guest molecules in their empty core for controlling the release.[2] They are widely exploited as protective containers for cells and enzymes, confined reaction vessels, carriers for drugs, heterogeneous catalysts, and dye dispersants.[2] Many of these applications require knowledge of the transport of molecules through these capsules. The understanding and control of small-molecule diffusion through the capsule is the basic requisite for many future applications, such as drug delivery systems and for biosensor development.[3]

Similar and very effective nanometer-sized containers, such as micelles and vesicular structures, are used by nature in biological systems. However, they have only a limited stability and may undergo structural changes.[4] Many applications require them to be more stable. In addition, most of the proposed applications are concerned with biology, so nanocapsules composed of biocompatible materials are also required.

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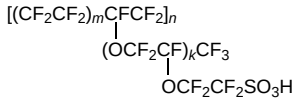
Nafion represents a novel and unique family of polyelectrolytes, which consist of a perfluorinated backbone and short pendant chains terminated by sulfonic head groups.[5] Various applications have been found in areas such as fuel cells,



Nafion

sensors, polymeric catalysts, membranes for separation, and purification.[6] Biocompatibility studies on Nafion have shown no acute or chronic foreign-body response.[7] Nafion possesses superselectivity, good mechanical properties, thermal stability (up to 200 °C), and chemical and biological inertness; this makes Nafion to one of the premier systems capable of operating in harsh biological environments.[8]

Electrostatic layer-by-layer self-assembly has been widely utilized to construct a variety of two- and three-dimensional multilayered structures.[9, 10] In this paper, we report the preparation of hollow capsules based on Fe^{3+}/Nafion by the sequential electrostatic deposition of the respective charged species onto colloid templates, followed by removal of the core. Photochemical bleaching and recovery of the capsule interior were used to determine the permeability of Fe^{3+}/Nafion multibilayers. A diffusion model is suggested to calculate the diffusion coefficient and to estimate the permeability of the Nafion capsule. The measurements give information on the dependence of the diffusion coefficient on the wall thickness.

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Experimental Section

Materials: Sodium poly(styrene sulfonate) (PSS, M_w 70000), poly(allylamine hydrochloride)(PAH, M_w 70000), Nafion, and iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) were purchased from Aldrich. Nafion was obtained as a 5% *w/v* mixture in water and lower aliphatic alcohols (1100 equiv. wt; i.e., 1100 g of polymer per mol of $-SO_3H$ groups). NH_4OH (28 wt%) and hydrochloric acid (37%) were used as a 1% dilution to adjust the pH. Polystyrene (PS, 240 nm, 10.55 μm) and melamine formaldehyde (MF, 4 μm) particles were purchased from Microparticles, GmbH, Berlin, Germany. Bis(dithiobenzil)nickel(II) tetra-*n*-butyl ammonium salt (BDTA) was synthesized previously.[11] Rhodamine-labeled PAH was prepared according to the literature.[12]

A solution of Nafion (1 mg mL^{-1}, 0.9 mM, based on the repeat unit molecular weight) was prepared by diluting the as-received solution in methanol/water (9:1). The pH, 3, of this solution was adjusted with aqueous $NH_3 \cdot H_2O$. The ionic strength of the Nafion solution was modified with KCl (0.01M). Then, a solution of $FeCl_3$ (5 mg mL^{-1}, 18.5 mM) was prepared by addition of $FeCl_3 \cdot 6H_2O$ (0.5 g) to water (100 mL; pH 2.0). Solutions of PAH (1 mg mL) and PSS (1 mg mL) in water with NaCl (0.5M) were prepared for all experiments.

Layer-by-layer self-assembly on colloid particles: Fe^{3+} and Nafion or PAH and PSS were assembled onto the surface of PS, MF, and BDTA microparticles by layer-by-layer adsorption according to the method reported.[9, 13] The added species with charge opposite to that of the particle surface or the last layer deposited was allowed to adsorb for 20 min. The excess polyelectrolytes or Fe^{3+} were removed by three repeated centrifugation (2000 g, 5 min)/washing/redispersion cycles with water in each deposition step. The subsequent layers were deposited in the same manner with the oppositely charged species. After completion of the desired number of deposition cycles, hollow capsules were prepared by dissolving the PS core with tetrahydrofuran, the MF core with HCl (0.1M), or the BDTA core with dimethylformamide. The resulting hollow polymer capsules were then centrifuged at 500 g for 5 min and washed with the corresponding solvent and water three times.

Characterization methods: The microelectrophoretic mobility of coated particles dispersed in pure water was measured with a Malvern Zetasizer 4. The mobilities u were converted into ζ potentials by using the Smoluchowski relation ($\zeta = u\eta/\varepsilon_0\varepsilon$), in which η and $\varepsilon_0\varepsilon$ are the viscosity and permittivity of the solution, respectively.

Absorption spectra of hollow capsules obtained by removal of the PS templates were measured in tetrahydrofuran on a Varian Cary 4E UV-visible spectrophotometer.

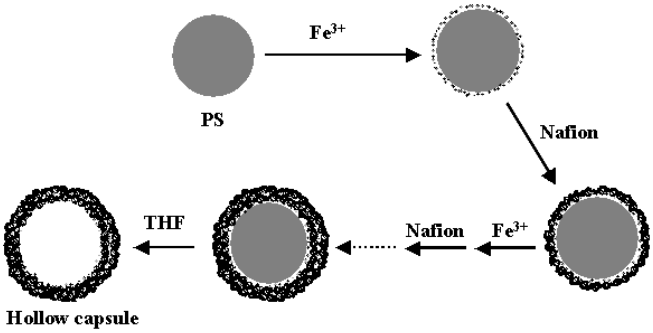
Confocal micrographs were taken with a confocal laser scanning microscope (CLSM) "Aristoplan" from Leica, equipped with a 100 × oil immersion objective.

The scanning force microscopy (SFM) images were obtained by means of a Digital Instruments Nanoscope IIIa in tapping mode. Samples were prepared by applying a drop of the capsule solution onto a freshly cleaved mica substrate. After the capsules had been allowed to settle, the substrate was dried naturally.

Photochemical bleaching and recovery (PBR) of the capsule interior were used to determine the permeability of Fe^{3+}/Nafion bilayers adsorbed onto the surface of hollow capsules of $(PSS/PAH)_3$ for fluorescein by means of CLSM (Ar/Kr laser, 488 nm). The diffusion coefficients of fluorescein through Fe^{3+}/Nafion bilayers were derived based on the assumption that hollow capsules of $(PSS/PAH)_3$ are permeable for small molecules and have negligible resistance compared with Nafion/Fe^{3+} bilayers. The laser beam was focused onto a spot inside the whole capsule. The interval between image scans varied depending on the duration of recovery. Recovery was considered complete when the intensity of the photobleached region stabilized. The fluorescence intensity was integrated by selecting a defined area in the interior.

Results and Discussion

Scheme 1 shows the general procedure of layer-by-layer self-assembly of Fe^{3+}/nafion onto the surface of PS latex particles. Nafion possesses a micellar conformation with the polar



Scheme 1. Illustration of the growth of alternating Fe^{3+}/Nafion capsules templated on PS latex particles with the neutral wash.

sulfonate groups located on the surface and the hydrophobic fluorocarbon backbone buried inside ($\varepsilon \approx 38$).[14] Nafion's acidity ($-H_o \sim 12$ on Hammett's scale) is comparable with that of 100% sulfuric acid;[15, 16] this implies a nearly complete degree of ionization at pH 3. Since adsorption of ferric ions onto the negatively charged surface of PS particles facilitates surface-charge reversal, the sulfonate groups of Nafion are attracted by ferric ions. The formation of insoluble hydroxides occurs during washing at pH ≥ 4.3 based on the solubility product of $Fe(OH)_3$ ($K_{sp} \sim 6 \times 10^{-39}$).[17] This transformation of adsorbed Fe^{3+} to $Fe(RSO_3)_x(OH)_{3-x}$ ($x = 1, 2, 3$; RSO_3 stands for Nafion) results in increasing basicity of the substrate and the formation of a cross-linked structure. The entire process is repeated until the desired number of deposition steps is achieved.

Following the successful buildup of multilayers and core removal, free-standing hollow capsules based on the Fe^{3+}/Nafion complex were obtained. Direct visualization of hollow capsules from Fe^{3+}/Nafion was provided by CLSM measurements, as shown in Figure 1. There is no evidence of a solid core, this indicates dissolution and removal of PS particles. The structures seen in the transmission image are due to the contrast of the remaining Fe^{3+}/Nafion complex layers from the original coating of templates. No closed capsule was

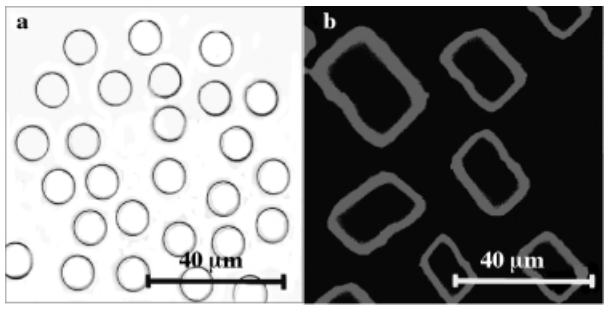


Figure 1. a) CLSM transmission image of capsules of $(Fe^{3+}/Nafion)_4$ templated on PS latex particles, b) CLSM fluorescence image of capsules of $(Fe^{3+}/Nafion)_4$ templated on BDTA microcrystals and after addition one layer of rhodamine-labeled PAH as the outermost one.

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obtained from one bilayer of Fe^{3+}/Nafion, but for the hollow capsules of more than one bilayer of Fe^{3+}/Nafion, the size and shape are persistent. This indicates that during core removal only a small osmotic pressure is transiently established and that the Fe^{3+}/Nafion complex can resist this pressure. Hollow capsules were also successfully fabricated by means of templating on MF latex particles and BDTA microcrystals, as well as $(PSS/PAH)_3$ hollow capsules. There is no basic difference on varying the kind of templates to start the self-assembly process. Essentially the first adsorbed layer has to possess a charge opposite to the particle surface.

The assembly of Fe^{3+}/Nafion or PAH/Nafion multilayers on PS colloid particles was followed by microelectrophoresis (Figure 2). Starting from -52 mV, corresponding to uncovered PS particles, the ζ potential alternates according to

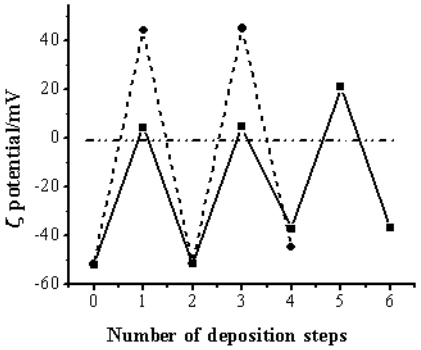

Figure 2. ζ potential of Fe^{3+}/Nafion (■) and PAH/Nafion (●) multilayers on 240 nm PS latex particles as a function of the number of deposition steps. The odd layer numbers correspond to Fe^{3+} or PAH deposition and the even layer numbers to Nafion adsorption. The uncovered PS latex particles exhibit a ζ potential of ca. -52 mV.

whether Fe^{3+} or Nafion formed the last adsorbed outer layer. Fe^{3+} as the outermost layer yielded ζ potentials from about 4 to 21 mV. Nafion as the outermost layer yielded ζ potentials from about -52 to -37 mV; this is consistent with a negatively charged particle surface.[18] These data demonstrate that the deposition of a metal ion, such as Fe^{3+}, with only three positive charges is effective in reversing the sign of the surface charge when deposited alternately with Nafion. For PAH/Nafion multilayers on PS spheres, the ζ potential alternated in a manner very similar to that reported for polyelectrolyte adsorption.[18] For both systems, the sign of the values obtained is in accordance with the charge on the species deposited, although Fe^{3+} yielded much smaller ζ potentials than PAH as the outermost layers.

To examine the deposition process of the Fe^{3+}/Nafion capsules in more detail, the deposition process was also monitored by UV-visible spectroscopy. The pronounced optical absorbance of ferric ions (bright yellow films) provides additional insight into the layer growth and degree of iron incorporation. Figure 3 shows UV/vis absorption spectra of Fe^{3+}/Nafion assemblies with different numbers of deposition steps. That the intensity developed with increasing number of adsorption cycles indicates a successful deposition. Thus, the UV/vis measurements also confirm the presence of Fe^{3+} in the capsules and support the microelectrophoresis results.

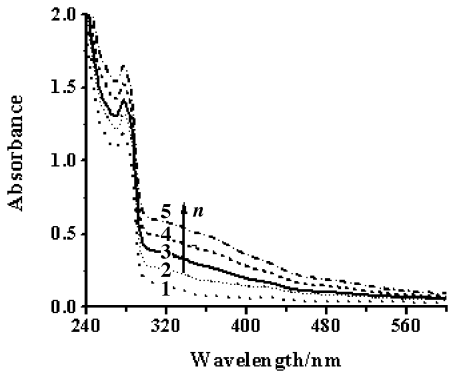

Figure 3. UV/vis absorption spectra of hollow capsules of $(Fe^{3+}/Nafion)_n$ ($n = 1, 2, 3, 4, 5$) obtained by removal of the 10.55 μm PS cores with THF. The resulting capsules were washed three times with THF and then redispersed in THF for measurements.

Hollow capsules typically maintain the spherical shape of the template particle in solution, while depositing them on a solid substrate and air-drying induce their collapse. Figure 4

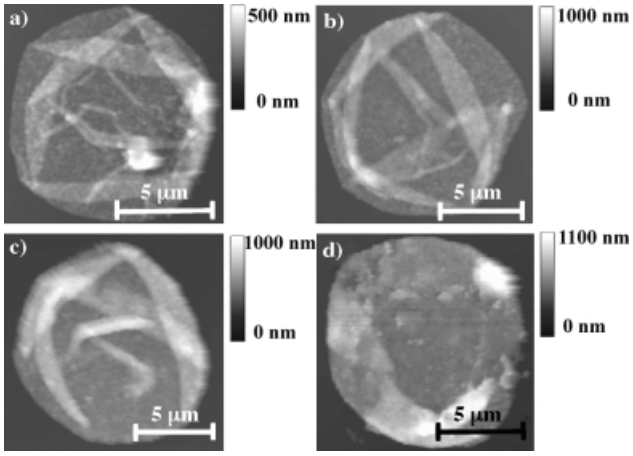

Figure 4. SFM images of capsules of $(Fe^{3+}/Nafion)_n$ templated onto 10.55 μm PS latex particles with neutral (pH 7) wash. a) $n = 2$, b) $n = 3$, c) $n = 4$, d) $n = 5$.

displays SFM images of capsules with different numbers of Fe^{3+}/Nafion bilayers templated onto 10.55 μm PS latex particles. A number of folds and creases were observed as a result of air-drying. Larger diameters than the template diameter were seen due to spreading effects. The capsules were found to be thicker with increasing number of Fe^{3+}/Nafion bilayers. In order to obtain quantitative evidence for the formation of Fe^{3+}/Nafion multilayers on the PS particles, the wall thickness of these capsules was determined from the smallest heights of the air-dried hollow capsules. This value is equivalent to twice the capsule-wall thickness. After the first few layers, the wall thickness increases almost linearly with the number of layers deposited (Figure 5). Such behavior has often been observed, with a few polyelectrolyte layers required prior to regular multilayer growth for films assembled by the layer-by-layer technique.[19] The average layer thickness for the Fe^{3+}/Nafion bilayer (calculated from the 6-, 8-, and 10-layer films) is 15.5 nm. This value is six times higher than the 2.6 nm observed in earlier studies for the thickness

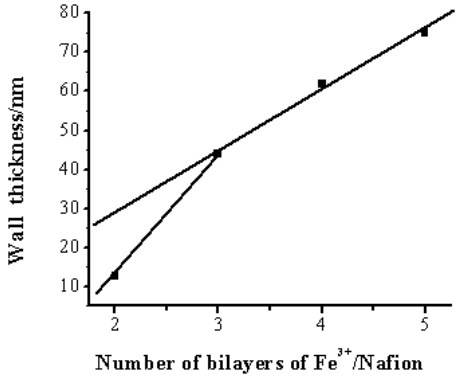

Figure 5. Thickness of capsule walls of $(Fe^{3+}/Nafion)_n$ ($n = 2$, 3, 4, 5) templated on 10.55 μm PS latex particles with neutral (pH 7) wash.

of bilayers of PSS/PAH.[20] Interestingly, there is a big difference between the wall thickness of the capsules of $(Fe^{3+}/Nafion)_4$ and $(PAH/Nafion)_4$ templated onto BDTA microcrystals with neutral wash. The thickness of a single Fe^{3+}/nafion bilayer of the former (24.8 nm) is much larger than that of the latter (15.6 nm). Overall, the microelectrophoresis, absorption spectroscopy, and microscopy data provide unambiguous evidence for the creation of hollow capsules from Fe^{3+}/Nafion and PAH/Nafion complexes with the layer-by-layer strategy.

The stability of the Fe^{3+}/Nafion hollow capsules with respect to pH value and heating was examined. In aqueous solution and over the course of one week, only a slight decrease in iron content (and subsequently Nafion) was observed, after this a constant value was reached for the duration of the experiment (6 weeks). According to integrated absorption spectra of the supernatant obtained by centrifugation of the capsule solution, the initial iron loss of about 5% is attributed to loosely attached Nafion moieties. After incubation in 10% NaOH and HCl (pH 1) for three months, no decomposition was observed; this indicates that Fe^{3+}/Nafion hollow capsules are stable over a wide pH range. On the other hand, capsules from PSS/PAH bilayers decompose at pH > 12. Raising the temperature may not facilitate the decomposition process. After heating Fe^{3+}/Nafion hollow capsules in water or NaCl (2 M) at 85 °C, or in ethylene glycol at 180 °C for 12 h, most of the capsules were still shape-persistent; this indicates that they are thermally stable.

In general, due to the sharp transition of adsorbed Fe^{3+} to $Fe(RSO_3)_x(OH)_{3-x}$ above pH 4.3, iron precipitation in neutral wash results in higher amounts of iron incorporation into the walls of the capsules and the formation of thicker walls than in acidic wash. Surprisingly, capsules obtained by using a neutral wash appear to be smoother and more uniform than those obtained with an acidic wash.

Figure 6 shows a typical PBR measurement by CLSM. Before bleaching and at low excitation intensity, equal emission is observed from inside and outside the capsule after incubation in fluorescein solution. On increasing the excitation intensity, the fluorescein is bleached within the illuminated area. Thus, the inside of the capsule becomes dark because unbleached fluorescein penetrates the wall too slowly. However, the fluorescence of the outside of the

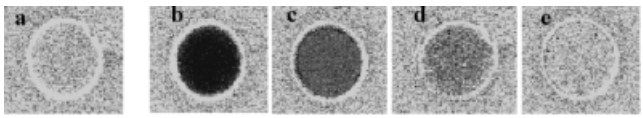

Figure 6. Typical photochemical bleaching and recovery of the fluorescence of fluorescein in the interior of $(PSS/PAH)_3$ capsules coated with three additional Nafion/Fe^{3+} bilayers. a) before bleaching, b) after bleaching, c–e) fluorescence recovery with time increased.

capsule exhibits almost no change. On decreasing the excitation intensity, the fluorescence recovery can be observed in the capsule interior as a function of time.

Figure 7 displays the fluorescence intensity in the capsule interior after a bleach pulse as a function of time for capsules coated with different numbers of Nafion/Fe^{3+} bilayers. As the

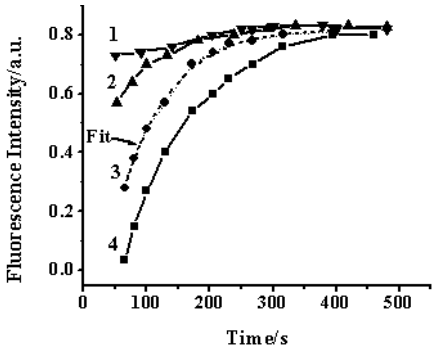

Figure 7. The fluorescence intensity in the capsule interior as a function of time after a bleach pulse for $(PSS/PAH)_3$ capsules coated with different (given) numbers of additional Nafion/Fe^{3+} bilayers.

number of Nafion/Fe^{3+} bilayers increases, the fluorescence recovery becomes slower and slower. The time dependence was fitted by a function:

$$I = c + a(1 - \exp^{-t/b}) \quad (1)$$

Equation (1) can expressed as a solution to Fick's law:

$$dC/dt = -A(C_0 - C) \quad (2)$$

Here C_0 and C represent the concentration outside and inside of the capsules, respectively, and C is proportional to the fluorescence intensity. The coefficient A is related to the diffusion coefficient (D) through a spherical wall with radius R and thickness L according to:

$$1/b = 3D/RL \quad (3)$$

According to Equation (3), a diffusion coefficient D can be calculated.[3a]

The Nafion micelles do not form a complete barrier for the fluorescein molecules, but they slow down their transport. The permeability is supposed to be caused by defects in the bilayer film. For the first and second layer assemblies, the large permeability might be attributed to the percolated pores of the supporting capsule wall. These pores progressively decrease in size, and by the third and fourth layer they are finally filled.[10] Thus, we have chosen the third and fourth bi-

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layers to calculate the diffusion coefficient, diffusion through which was determined to be 4.1×10^{-12} and 3.8×10^{-12} $cm^2 s^{-1}$, respectively, based on the radius $R = 2$ μm. Galeska et al. derived a diffusion coefficient for glucose for through Fe^{3+}/Nafion in the order of 10^{-10} $cm^2 s^{-1}$.[10] Differently from in normal capsules of $(PSS/PAH)_4$, annealing results in higher fluorescein permeability for capsules of $(Fe^{3+}/Nafion)_4$; this can be attributed to increased porosity. Annealing modifies the microstructure by inducing hydrophilic channels in the Nafion assembly, thereby facilitating transport of fluorescein through the walls.[21]

Conclusion

We have described an effective method for the fabrication of biocompatible Nafion-based hollow capsules. Iron precipitation in neutral wash results in higher $Fe^{3+}/Fe(OH)_{1\text{-}3}$ incorporation into the walls of the capsules. The demonstrated hydrolytic stability of these Nafion/Fe^{3+} capsules over a wide range of pH and at high temperature is of great importance for many applications. A diffusion model was used to estimate the permeability of Nafion/Fe^{3+} capsules for small fluorescein molecules. The method can be generalized to other systems. A diffusion coefficient of Nafion/Fe^{3+} capsules for fluorescein was derived in the order of 10^{-12} $cm^2 s^{-1}$. The permeability can be manipulated by changing the number of Nafion/Fe^{3+} bilayers. We expect the novel Nafion capsules to be of particular interest for applications such as drug transport and release, and biosensors—for which controlled diffusion for small molecules, biocompatibility and remarkable stability are most important.

Acknowledgements

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