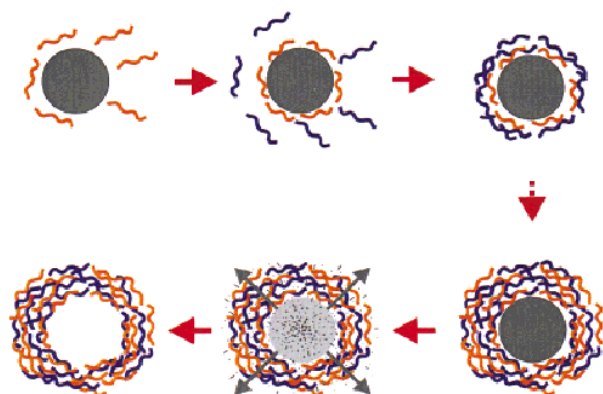


## Exploring novel polyelectrolyte capsules with atomic force microscopy

### Introduction

Using capsules as micro- and nanocarriers for molecules and nanoparticles has been extensively studied during the last decade [1]. In contrast to liposomes, polyelectrolyte capsules are permeable for polar molecules and are much more chemically and physically resistant. Organic and inorganic particles, oil droplets and even biological cells can be used as templates for capsule fabrication.



**Fig. 1** Schematic drawing of the formation of water filled polyelectrolyte capsules. A shell is formed around a template in a process of alternating layer by layer deposition of positively and negatively charged polyelectrolytes. After chemical removal of the template, a water filled capsule remains. Illustration after [1].

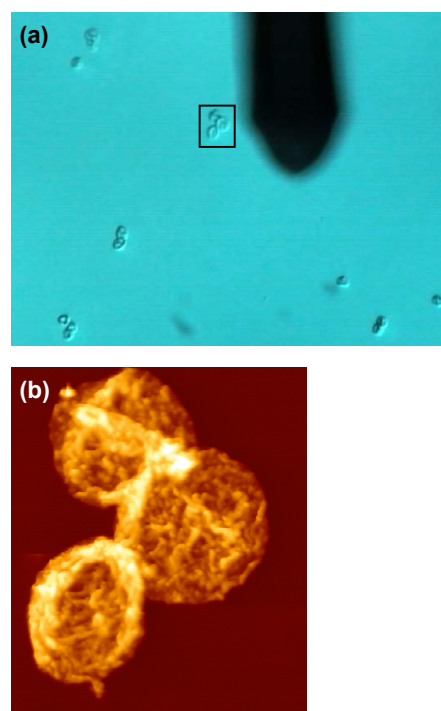
The size of the resulting capsules strongly depends on the template employed. In a stepwise process, alternating polyanionic and polycationic polymers are added to the particle suspension leading to multiple polyelectrolyte layers. After removal of the core, a hollow, water-filled capsule remains, as shown schematically in Figure 1. Depending on the core substrate size, the capsules can be made in the nanometer to micron range. The thickness of capsules can be adjusted by the number of layers deposited on the template and is in the nanometer range.

### Shell preparation

In this study, shells were prepared according to a procedure described in [1]. As a template, manganese carbonate particles of 3.6 to 4 microns in diameter were

suspended in water at a concentration of 25 mg/mL. A layer by layer deposition of all in all 8 layers was used for shells fabrication. Poly(allylamine), poly(ethylenimine) and poly(diallyldimethyl ammonium) chloride were used as positively charged polyelectrolytes. Poly(1-(4-(3-carboxy-4-hydroxyphenylazo)-benzene sulfonamide)-1,2-ethanediyl) sodium salt served as polyanion.

The suspension was centrifuged and washed several times after each adsorption step in order to remove excess of polyelectrolyte. The inner carbonate core is removed with 0.1 M HCl, the decomposition of carbonate particle can be observed by seeing the suspension becoming transparent. The shell suspension was centrifuged and thoroughly washed with ultraclean water several times.



**Fig. 2** Optical (a) and corresponding AFM image (b) of the shell sample. The optical image was obtained in transmitted light DIC, the AFM scan region is marked. AFM image size is 11 x 12.1  $\mu\text{m}$ , the height range is 500 nm.

### Imaging Methods

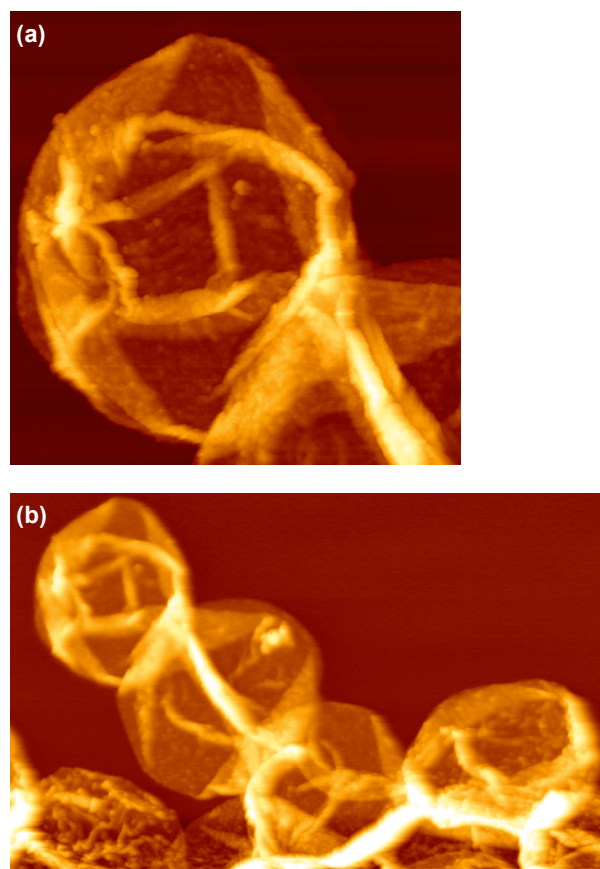
The shell suspension was poured onto PEI coated microscopy glass slides, incubated for adsorption for 20 minutes, washed with ultraclean water and dried in a nitrogen flow leading to a surface coverage of approximately 1000 shells per mm<sup>2</sup>, leaving most of the substrate clear of shells (see the optical image in Figure 2). This meant that the time searching for groups or single shells could be minimized by combining AFM with optical microscopy. Suitable shell samples could then be chosen in transmitted light DIC contrast prior to scanning. AFM images were obtained at room temperature with a JPK NanoWizard® in the Life Science version. The AFM head was placed onto a Zeiss Axiovert 200 inverted optical microscope.

The shells are delicate and brittle and can easily be damaged mechanically if the force exerted is too high. Macroscopic damage of the shells can clearly be observed in the optical microscope. AFM images were obtained in intermittent contact mode with standard silicon non-contact cantilevers (NCH) provided by Nanoworld, Switzerland. Resonance frequency was ~ 300 kHz, spring constant ~ 40 N/m. Digital resolution was 512 x 512 pixels.

### Results and Discussion

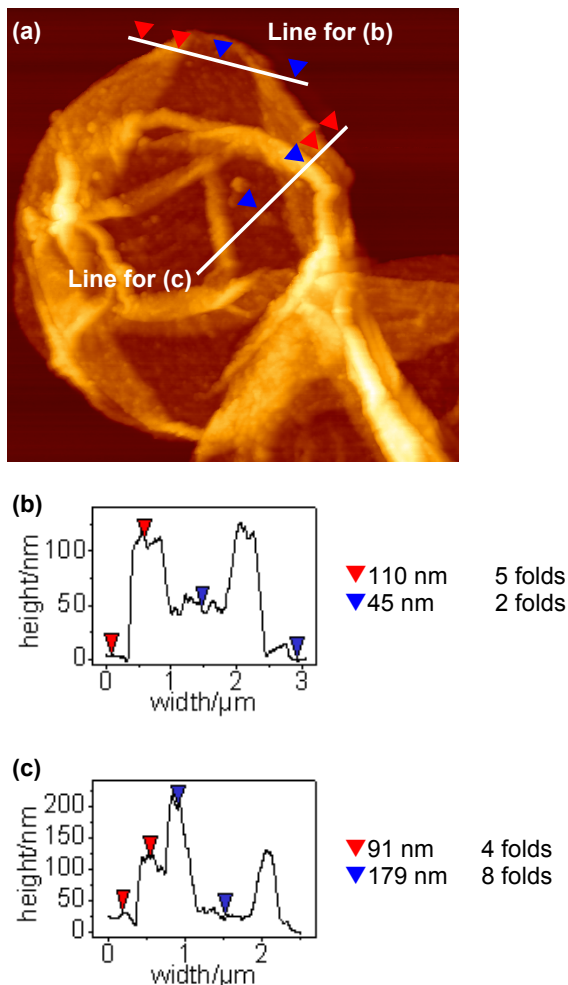
In the AFM image the outer shape of the shells looks folded and creased. Their former round shape as seen on confocal microscopy images of comparable capsules in [2] is more polygonal after the drying process as shown in Fig. 3 a. Drying the shells in air leads to vaporization of the inner water and, therefore, the shells collapse. Size and shape distribution is rather homogeneous. Most capsules are in the range of 4 to 5 µm in diameter, which is larger than the untreated MnCO<sub>3</sub> particles. Capsules stick together upon drying due to hydrophobic effect.

The average thickness of the shells is approximately 300 nm. Darker domains in the AFM image can be seen as a superimposition of two shell walls caused by their collapse. Brighter spots in the image are supposed to be some residue of carbonate particles as mentioned in [2].



**Fig. 3** (a) Dried polyelectrolyte shell consisting of 8 polyelectrolyte layers, image 5.2 x 5.2 microns, z-range 300 nm, imaged in intermittent contact mode. (b) Overview image, scanned prior to Fig. 3 a, 9.5 x 15 µm, z-range 300 nm.

By evaluating the height of the collapsed capsule, the thickness of a single polymer layer can be calculated. In Figure 4, height profiles are evaluated. Figure 4 (a) shows the lowest step that can be found on the shell, indicating two shell membranes lying on top of each other. This corresponds to the thickness of 16 polyelectrolyte layers. So the thickness of a single layer can be estimated. The height of the lowest step is 45 nm leading to the thickness of a single layer of 2.8 nm or 22.4 nm for a whole shell membrane. The other heights estimated from height profiles of 4 (a) and 4 (b) show heights being integer multiples of 22.4 nm. While even multiples are favoured odd multiples can also be explained topologically.



**Fig. 4** Measuring the height profiles shows that the height of the folds found on the shell is integer multiples of a single shell wall thickness.

The wall thickness can also be measured by light scattering experiments. The light scattering approach is based on calculations that use the optical density of polyelectrolyte layers, which is unknown in most cases. In contrast, atomic force microscopy gives the directly observed value for the membrane's thickness immediately without needing further determination of physical constants.

### Acknowledgement

Shell samples were prepared by Alexei Antipov, member of Gleb B. Sukhorukov's group at Max-Planck-Institute of Colloids and Interfaces, Am Mühlenberg 1, 14476 Golm. <http://www.mpikg-golm.mpg.de/gf/gleb/index1>

### Literature

- [1] E Donath, G B Sukhorukov, F Caruso, S A Davis, H Möhwald. Novel hollow polymer shells by colloid-templated assembly of polyelectrolytes. *Angew. Chem. Int. Ed.* 37 (1998) 2201-2205.
- [2] S Leporatti, A Voigt, R Mitlöchner, G Sukhorukov, E Donath, H Möhwald. Scanning force microscopy investigation of polyelectrolyte nano- and microcapsule wall texture. *Langmuir* 16 (2000) 4059-4063.