Functional Materials

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Structural characterization of polyelectrolyte multilayer hollow capsules by SEM

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Polyelectrolyte hollow capsules are promising material that can be used for example as a drug delivery system in medical applications and release applications [1]. They can be prepared from polyelectrolytes on silica spherical particles by using the layer-by-layer self-assembly method [2] and, consequently, dissolving the silica core with dilute hydrofluoric acid. Poly(allylamine hydrochlorid) (PAH) and poly(sodium 4-styrene sulfonate) (PSS) were used as a base material for the wall of the capsules. The capsules presented here with a diameter of ~400 nm consist of 5 bilayers of PAH/PSS polyelectrolytes (Figure 1a). The wall permeability is a crucial property for, e.g., drug delivery applications, and can be readily measured by confocal laser scanning microscopy and nuclear magnetic resonance diffusion experiments [3]. Dimensions of our capsules are rather small in comparison to typically studied ones, and therefore, electron microscopy is essential tool for detailed structure characterization.

A high-resolution field-emission scanning electron microscope was employed to investigate the structure details of the capsule wall. The capsules before the core dissolution process were investigated in the air-dried state. Both secondary electron (SE) and back-scattered electron (BSE) micrographs were recorded simultaneously (Figure 1b). The BSE micrograph may be used for rough estimation of the thickness of the capsule wall, since the density of silica core is ~2 times higher than the density of the polyelectrolyte wall. Monte Carlo simulations of electron scattering in planar films show that at 20 keV electron energy the BSE yield from silica is ~3 times stronger than that from polymeric materials.

Because the hollow capsules are damaged during their air-drying process due to the surface tension forces, cryo-techniques had to be employed. Here, we used the freeze-drying techniques developed and used mainly for investigations of biological samples [4] to retain the intact shape of the capsules. Capsules were rapidly frozen into liquid ethane, subsequently freeze-dried at vacuum, and finally rotary coated with very thin metal layer for high-resolution imaging (Figure 1c). This technique allowed for the first time to observe the capsules at high resolution in their intact shape and enabled to find new features, e.g., holes within size ≥10 nm in their capsule wall [5].

In addition, a quantitative annular dark-field (ADF) imaging mode [6-8] is applied for quantitative investigations of the mass-thickness mapping of the wall using the high-resolution SEM S-5000 (Hitachi, Japan) in the transmission mode. The first images (Figure 1d) prove the clear dependence of the ADF signal to the thickness wall.

1. A.L. Becker et al., Small 6 (2010), p. 1836.
2. G.B. Sukhorukov et al, Polym. Adv. Technol. 9 (1998), p. 759.
3. R.P. Choudbury et al., J. Phys. Chem. B 112 (2008), p. 13245.
5. A. Cavalier et al, “Handbook of Cryo-Preparation Methods for Electron Microscopy”, CRC Press, Boca Raton 2009.
6. V. Krzyzanek et al., Soft Matter 7 (2011), p. 7034.
7. V. Krzyzanek and R. Reichelt, Microscopy & Microanalysis 13 (Suppl. 3) (2007), p. 80.
8. H. Nusse et al., in Proc. Microscopy Conference MC2011, Kiel (2011).
9. S. Tacke et al., in Proc. Microscopy Conference MC2013, Regensburg (2013).
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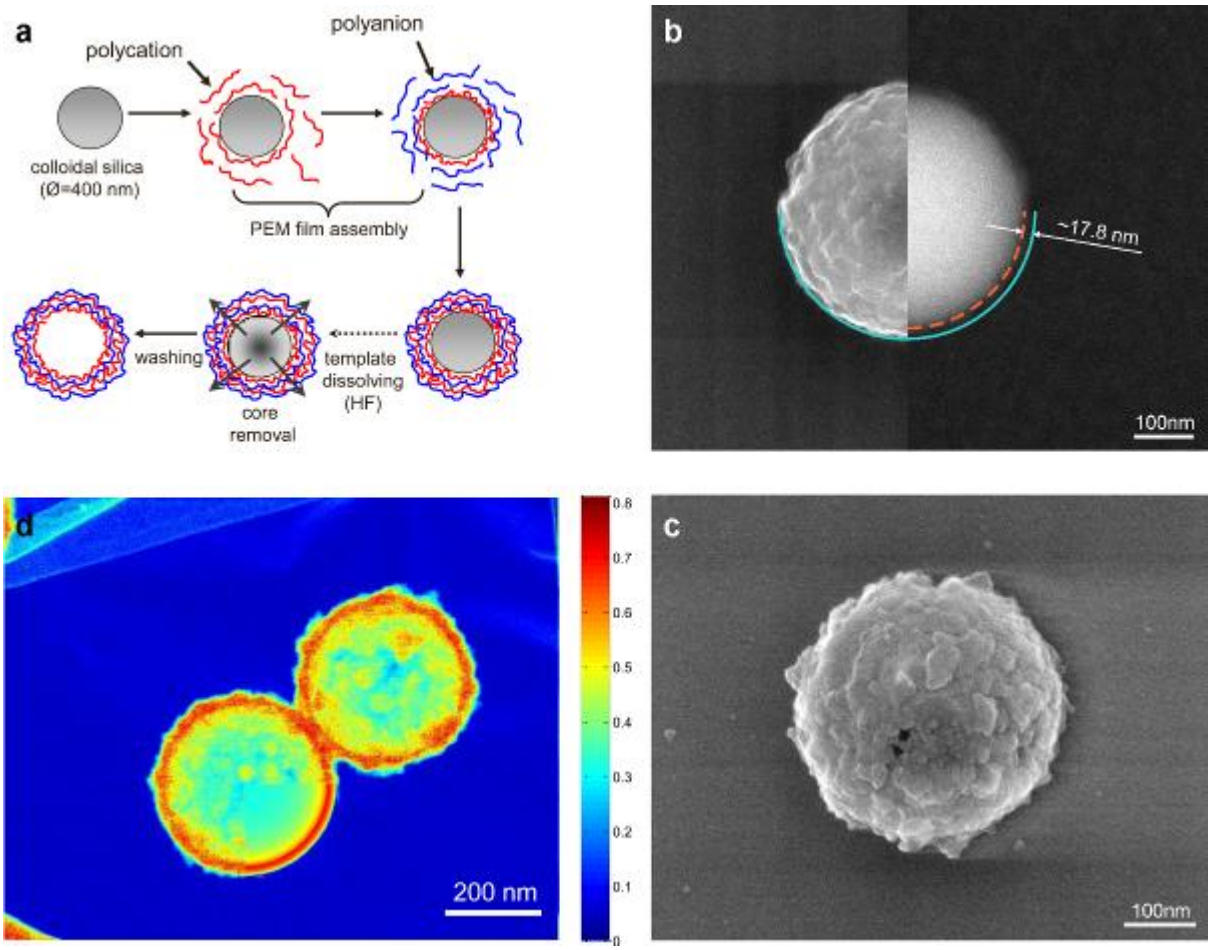

Figure 1. Polyelectrolyte multilayer hollow capsules: (a) Graphical illustration of the capsule preparation. (b) Air-dried hollow capsules before dissolving the core: SE (left half) and BSE (right half) micrographs acquired simultaneously. The BSE micrograph may be used for a rough estimation of the thickness of the capsule wall; the dashed red line indicate the core/wall interface and the solid green line indicate the wall/vacuum interface, respectively. (c) SE micrograph of freeze-dried hollow capsule. (d) ADF micrograph of hollow capsules on very thin amorphous carbon film recorded at very low electron dose; the colour scale is recalculated to the fraction of elastically scattered electrons, the right bottom segment is a theoretical model.