

## CORE/SHELL CAPSULES FORMED BY SILICA PRECIPITATION IN BIOPOLYMER COACERVATE SCAFFOLDS

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Delivery systems with low-permeability barriers and controllable release are crucial for the encapsulation of cells, pharmaceuticals, vitamins, inks, or fragrance and flavor molecules [1-3]. Here, we describe core/shell capsules with dense walls composed of a biopolymer scaffold and interpenetrated by a network of amorphous silica. We first generate a weakly acidic hydrogel shell around an oil drop via interfacial deposition of complex coacervates, formed by phase separation of a protein with a weakly anionic polysaccharide. Following covalent crosslinking of the protein component in the coacervate gel, this shell then serves as a scaffold to induce protein-directed mineralization of silicon dioxide from a liquid-silica precursor.

The precipitation process occurring in the hydrogel scaffold of the capsule shell simultaneously consumes water and forms silica, yielding dense shells with a very low permeability for volatile organic compounds and adjustable mechanical characteristics. We use solid state CP/MAS  $^{29}\text{Si}$  NMR spectroscopy to characterize the silica/biopolymer hybrid shells and find a high fraction of interfacial silanol groups, associated with a large internal surface area of the inorganic silica phase. Combined with specific surface area measurements, thermogravimetry, SEM imaging and energy-dispersive X-ray spectroscopy (EDS) of the shells, these data reveal a composite shell material wherein the precipitated silica interpenetrates the crosslinked coacervate scaffold [1].

To evaluate the core/shell capsules as delivery systems for low molecular weight volatile payloads, we perform mechanical testing on ensembles of individual capsules to compare the stiffness, modulus and rupture behavior relevant for mechanically-driven release. Furthermore, we investigate the role of three-phase wetting phenomena at the coacervate/oil/water interface during the formation of the core/shell structure using rheology and an analysis of interfacial stresses [2], accounting for both capillary forces and viscoelastic effects.

The co-continuous silica/coacervate shells created here have outstanding barrier and mechanical properties, even for encapsulation of relatively small volatile molecules. As a specific example, we encapsulated model volatile fragrance molecules for protection against evaporation and degradation and demonstrate mechanically triggered release upon fracture. More generally, this method is applicable to a wide range of chemical systems provided their oil/water partition coefficients allow to form an initial oil-in-water emulsion.

[1] P Erni, G Dardelle, W Fieber et al. (2013), *Angew Chem - Int Ed*, 52, 10334.

[2] G Dardelle, P Erni (2014), *Adv Colloid Interface Sci*, 206, 79.

[3] G Dardelle, M Jacquemond, P Erni (2016), *in press*.