Cellulose-coated emulsion microparticles with a unique inner hydrogel shell: structure and function as micro-reactors for enzymatic transformations

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Cellulose is an abundant and renewable resource for sustainable chemicals and fuels. We developed cellulose-coated emulsion microparticles fabricated by high-pressure homogenization of the oil with an aqueous suspension containing cellulose hydrogel particles. The cellulose hydrogel is regenerated from aqueous alkali solution by coagulation with water and further washing. The inner structure of these micro-particles was revealed by imaging using cryogenic scanning electron microscopy and quantified by small-angle x-ray scattering: a unique multi-layer structure in which an inner oil core is surrounded by a shell composed of a porous cellulose hydrogel, which is encapsulated by an external cellulose shell. The outer coating appears to be homogeneous without evidence of particulate matter, indicating that the emulsion is not of the "Pickering" type. The inner shell is determined to be a porous cellulose hydrogel which is inhomogeneous. It consists of pores, the size of which is a few tens of nanometers, embedded in a denser highly branched hydrogel with an apparent fractal structure. The fractal dimension (~2.5) is suggestive of the aggregation process that occurs during regeneration.

Our objective is to convert cellulose from pretreated biomass directly to bioethanol and biodiesel in a one-pot process using these microparticles as bio-reactors for a cascade of biochemical processes. We show that enzymes can be spontaneously incorporated with these microparticle: cellulytic enzymes attach to the outer layer while lipases spontaneously penetrate the inner shell to reside at the inner oil-hydrogel interface. Moreover, the cellulose-coated emulsion microparticles spontaneously hybridize with yeast cells (*S. cerevisiae*). We show that this integrated structure is effective in simultaneous cellulose saccharification and fermentation to ethanol. Furthermore, we recently demonstrated the full "one-pot" transformation of cellulose to fatty-acid ethanol ester ("biodiesel") by enzymatic cellulose hydrolysis, yeast fermentation and lipase-catalyzed trans-esterification of triacyl-glyceride in the microparticles' core, in a single emulsion-based consolidated bioprocess.