Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Nanoassembly of Biocompatible Microcapsules for Urease Encapsulation and Their Use as Biomimetic Reactors

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Materials. Urease (M_W ~48,000), poly(l-lysine) hydrobromide (PLL, M_W 30,000 – 70,000 g/mol), Poly(l-glutamic acid) (PGA, M_W 50,000 – 100,000 g/mol), urea, $CaCl_2$, 2-(N-morpholino)ethanesulfonic acid (MES), hydrofluoric acid (HF), ammonium fluoride (NH_4F), sodium metasilicate (Na_2SiO_3), tetraethyl orthosilicate (TEOS, 98%), di(methylsulfoxide) (DMSO) were obtained from Sigma-Aldrich and used as received. Bimodal mesoporous spheres (MS) of diameter approximately 2-4 μm, total surface area 630 m^2g^{-1} and pore volume 1.72 ml g^{-1}, were synthesized as via the literature[5]. 1 mg mL^{-1} PLL and PGA solutions were prepared in 0.05 M pH 5.5 MES buffer solution. The solution used for dissolving silica core is a mixture of 2 M HF and 8 M NH_4F at a pH ~ 5. The water used in all experiments was prepared in a Millipore Milli-Q purification system and had a resistivity higher than 18.2 MΩ cm.

Enzyme loading and encapsulation. Approximately 5 mg of the MS particles were incubated with 1.5 mL 2 $mg.mL^{-1}$ of urease solution (in pH 5.5 MES buffer) at 5 °C for 3d with initially sonication for 5 minutes to disperse the silica particles. After

adsorbing, the enzyme-loaded particles were separated and washed with chilled (5 °C) MES buffer twice via centrifugation (500 *g* for 5 min). The urease amount that retained in the particles was measured by Standard Micro BCA^{TM} Protein Assay kit (Pierce, Product No. 23209). The coating of PLL and PGA on enzyme adsorbed MS particles was then performed by adsorbing in 1 mg mL^{-1} PLL or PGA solutions (fleshly prepared in 0.05 M pH 5.5 MES buffer, 5 °C) for 10 min, with occasional shaking, and excess polymers were separated by three centrifugation (500g for 5 min)/redispersion cycles using pH 5.5 MES buffer solutions. These processes were repeated until three bilayers (PLL/PLGA) were coated.

Characterization. Scanning Electron Microscopy (SEM) samples were prepared by placing a drop of diluted sample suspension (dispersed in water) onto a cleaned microscopy glass. After coating with a thin layer of platinum, SEM images were recorded with a JEOL JSM 6400F instrument at an acceleration voltage of 10 kV. A Perkin Elmer FTIR spectrometer 2000 was performed for FTIR measurement. XRD measurements were carried out at a MiniFlex XRD instrument (Rigaku Co.).

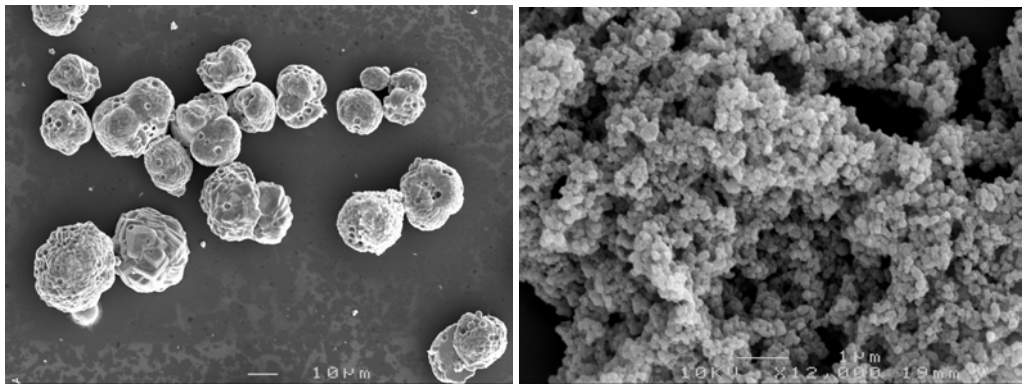

Figure S1. SEM images of urease-loaded $(PLL/PGA)_3$ capsules after carbonate precipitation in 0.5 M urea and 1M $CaCl_2$ solution for 24 h (left) and calcium carbonate precipitates obtained in a solution containing 0.5 M urea, 1 M $CaCl_2$ and 30 $mg.mL^{-1}$ urease (right) without PE capsules.

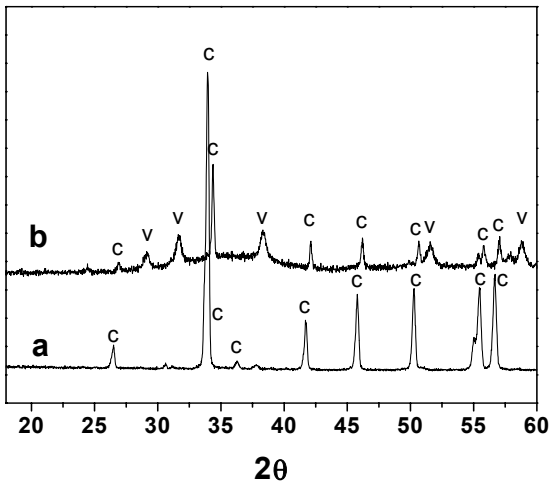

Figure S2. XRD patterns of calcium carbonate precipitates obtained in a solution containing 0.5 M urea, 1 M $CaCl_2$ and urease at a concentration of 0.3 $mg.mL^{-1}$ (a) and 30 $mg.mL^{-1}$ (b). Samples were separated from the reaction solution and washed with water by centrifugation and dried overnight under vacuum. Peaks coded as C and V, respectively, are characteristic of calcite and vaterite.