Electronic Supplementary Information (ESI)

Peptide-Catalyzed, Bioinspired Silicification for Single-Cell Encapsulation in the Imidazole Buffer System

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Experimental Section

Catalytic Activity Test of $R_4C_{12}R_4$ in Solution. The aqueous stock solution (1 mg/mL) of $R_4C_{12}R_4$ was prepared for the quantitative analysis of polymerized Si. The concentraton of $R_4C_{12}R_4$ was set to be 0.1 mg/mL in Tris, phosphate, or imidazole buffer (pH 7.4; final concentration: 50 mM). As a control, the imidazole-buffered solution without the peptide was prepared. To the peptide solution was added TEOS (10 mM), and the mixture was stirred gently. After 6 h, precipitates were collected by centrifugation and washed with ethanol three times. The precipitates were dissolved in 2 M NaOH, and the resulting solution was placed immediately in a water bath at 80 ^oC for 60 min. The spectrophotometric silicomolybdic acid assay was performed according to the previous report (C. C. Perry *et al*., *Langmuir* 2011, **27**, 15135).

$R_4C_{12}R_4$-Catalyzed Formation of Silica Films on Gold. A gold-coated silicon wafer (with 5 nm of a titanium adhesion layer and 100 nm of thermally evaporated gold layer) was cut into small pieces (1 cm × 2 cm) and cleaned with piranha solution. The gold substrates were immersed for 16 h in an ethanolic solution (1 mM) of 16-mercaptohexadecanoic acid to form self-assembled monolayers (SAMs) terminated with carboxylic acid. The SAM-coated gold substrate was immersed in an aqueous peptide solution (1 mg/mL) for 10 min, washed with deionized water, and dried under a stream of argon. The peptide-adsorbed gold substrate was placed in the imidazole-buffered solution (50 mM, pH 7.4), followed by addition of TEOS (50 mM). After 6 h, the substrate was taken out, washed with deionized water and ethanol, and dried under a stream of argon.

Cell Encapsulation. A single colony of yeast cells was picked from a yeast-extract-peptone-dextrose (YPD) broth agar plate, and suspended in the YPD broth and cultured in a shaking incubator at 30 ^oC for 30 h. The cells were washed with 0.15 M aqueous NaCl solution and deionized water. The aqueous $R_4C_{12}R_4$ solution (1 mg/mL) was prepared for the peptide adsorption. To the cell pellets was added the peptide solution, and the resulting solution was stirred gently for 10 min. The peptide-adsorbed cells were washed with deionized water three times to remove the unabsorbed peptide. The cell pellets were suspended in the imidazole-buffered solution (50 mM, pH 7.4), and TEOS (final concentration: 10, 50, or 100 mM) were added with magnetic stirring. After 6 h, the encapsulated cells (yeast@SiO_2) were washed with 0.15 M aqueous NaCl solution and deionized water three times. Before cell-growth monitoring, the optical density of native yeasts or yeast@SiO_2 was adjusted to ~1.0 at 600 nm by dilution with 0.85% aqueous NaCl solution. The 10 μL of the yeast mixture was suspended in a YPD broth and cultured in a shaking incubator at 30 ^oC. The small amount of the mixture was picked at the predetermined time, and the optical density was measured at 600 nm by UV-visible spectroscopy.

Viability Test. The viability of yeast cells was measured by using fluorescein diacetate (FDA). The stock solution of FDA was prepared by dissolving FDA in acetone (10 mg/mL), because FDA was poorly soluble in water. The 2 μL of the stock solution was mixed with 1 mL of yeast cell suspension (pH 6.5, 10-mM phosphate buffer solution). The suspension was incubated for 30 min at room temperature while shaking, and then the cells were collected by centrifugation, washed with water, and characterized by laser scanning confocal microscopy.

Cell-Lysis Test. The stock solution of lyticase was prepared by dissolving lyticase (~3.8 mg, ≥ 2,000 units/mg protein, from Arthrobacter luteus) in a mixture of glycerol (500 μL) and Tris-EDTA (TE) buffer solution (500 μL, pH 7.5). The 10 μL of the stock solution was added

to the yeast suspension (TE buffer solution, pH 7.5), and the suspension was incubated while shaking at 37 ^{o}C. The small amount of the mixture was picked at the predetermined time, and the optical density was measured at 600 nm by UV-visible spectroscopy.

Characterizations. Scanning electron microscopy (SEM) imaging and energy-dispersive X-ray (EDX) spectroscopy elemental analysis were performed with an Inspect F50 and a Nova230 microscope (FEI Co., the Netherlands) after sputter-coating with platinum. IR spectra were recorded in single reflection mode by using a dry N_2-purged Nicolet FTIR spectrophotometer (Thermo Scientific, USA) equipped with the smart SAGA (smart aperture grazing angle) accessory. The film thickness was measured with a Gaertner L116s ellipsometer (Gaertner Scientific Corporation, USA) equipped with a He-Ne laser (632.8 nm) at a 70^{o} angle of incidence. A refractive index of 1.46 was used for all the films. The cells were observed with an LSM 700 confocal microscope (Carl Zeiss, Germany).

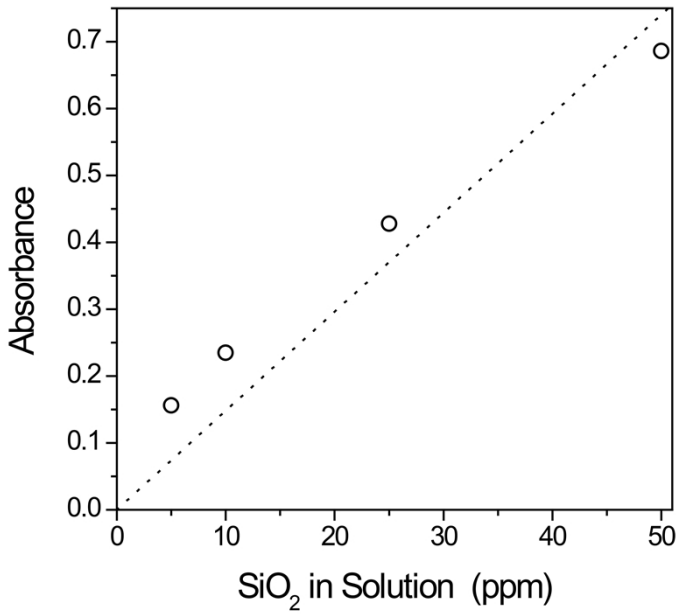

Fig. S1 Linear standard curve of UV-Vis absorbance at 810 nm vs. the concentration of silica.

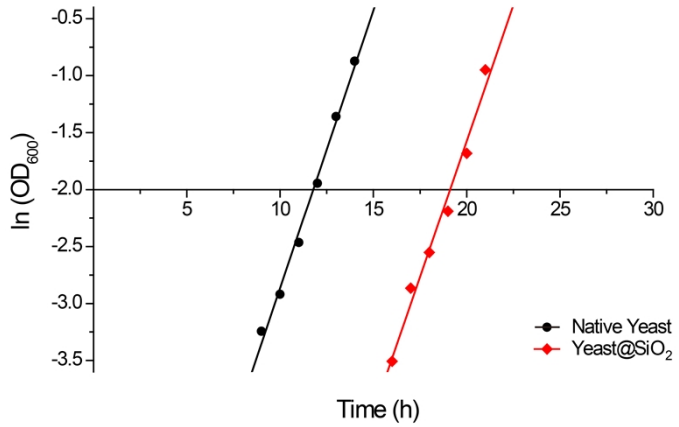

Fig. S2 Linear-fitted plots of ln(OD_{600}) vs. time for native yeast and yeast@SiO_2.

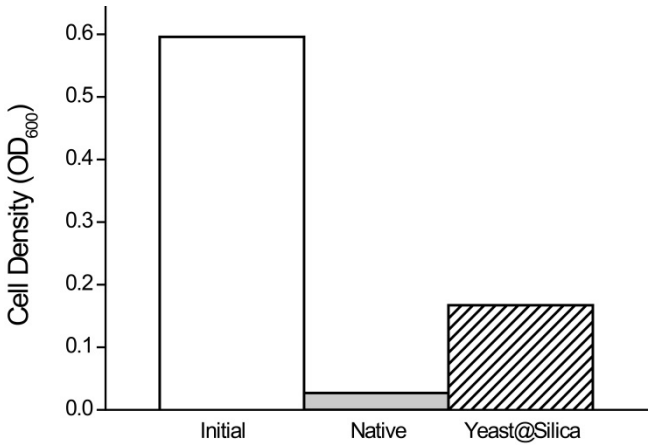

Fig. S3 Observed cell density (OD_{600} value) for native yeast and yeast@SiO_2 after 30-min treatment of lyticase.