Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Polydopamine Nanocoated Whole-Cell Asymmetric Biocatalyst

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Methods

Polydopamine coating. A single colony of yeast cells *Rhodotorula glutinis* was picked from a potato dextrose agar plate, and suspended in the yeast-extract-peptone-dextrose (YPD) broth and cultured in a shaking incubator at 180 rpm at 32 ^{o}C for 36 h. 50 mL mixture was centrifuged and washed with a tris(hydroxymethyl) aminomethane (TRIS, Sigma-Aldrich, USA) buffer (50 mM, pH 8.0). The cells were immersed and shaken gently in 10 mL TRIS buffer solution (pH 8.5, 50 mM) of 3 mg/mL dopamine hydrochloride (Sigma-Aldrich, USA) for 3 h. The cell@PDA were washed with a TRIS buffer (50 mM, pH 8.0) and collected with centrifugation. When the experiments required, cell@PDA were cultured as described above, utilized for the surface post-functionalization or applied for the asymmetric reduction. PDA particles can be synthesized by shaken gently 10 mL TRIS buffer solution (pH 8.5, 50 mM) of 3 mg/mL dopamine hydrochloride (Sigma-Aldrich, USA) for 3 h.

Characterization. Scanning electron microscopy (SEM) were performed using a JEOL 7550F (JEOL, Japan), operated at 15 kV. For specimen's preparation, cells were dehydrated in a series of solutions with increasing percentages of ethanol and supercritically dried in a Leica EM CDP030 (Leica, Germany). Transmission Electron Microscopy (TEM), High Angle Annular Dark Field Scanning Transmission Electron Microscopy (HAADF-STEM), and Energy Dispersive X-ray spectroscopy (EDX) were performed on a FEI Tecnai Osiris

fitted with Super-X windowless EDX detector system, operated at 200 kV. Specimens sections for TEM were prepared by fixing encapsulated cyanobacteria with gluteraldehyde, OsO_4, followed by dehydration in acetone and embedding Epon 812/Araldite M resin. Subsequently, thin sections were cut using a ULTRACUT UCT ultramicrotome (Leica, Germany). Confocal laser scanning microscopic (CLSM) images were acquired by using a Leica TCS SP5 (Leica, Germany). The magnetization of the native cells and encapsulated cells were measured by using a Physical Property Measurement System (PPMS, Quantum Design, USA) at 300 K. X-ray diffraction was performed using a Philips PW 1820 diffractometer (Philips, The Netherlands), operated at 40 kV and 30 mA. UV-visible spectra were measured by using a Perkin-Elmer Lambda 35 spectrometer (Perkin-Elmer, USA).

Cell viability tests. The viability of cells prior to and after encapsulation was measured by using LIVE/DEAD® Yeast Viability Kit (L-7009, Thermo Fisher SCIENTIFIC, USA) which combines a two-color probe for yeast viability, FUN1®, with a fluorescent fungal surface labeling reagent Calcofluor® WhiteM2R. The cells were fluorescence labeled by the protocol of LIVE/DEAD® Yeast Viability Kit. Firstly, 100 µL of the cell culture was added to 1 mL 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES, Sigma-Aldrich, USA) buffer (pH 7.4, 10 mM) containing 2% D-(+)-glucose (Sigma-Aldrich, USA), harvested by centrifugation for 5 min at 10000 g and

resuspended in 1 mL the HEPES buffer. Subsequently, the cell suspension was combined with FUN1® cell stain and Calcofluor® WhiteM2R cell staining solution. The final concentration of FUN1® cell stain was 10 μM and the Calcofluor® WhiteM2R was at a final concentration of 25 μM. Finally, the mixture was incubated at 30 ^{o}C in the dark for 30 min and subsequently examined by using CLSM.

Cell growth monitoring. Growth kinetics was evaluated by suspending cell or cell@PDA in medium (YPD broth) to an OD595 nm of 0.1 and monitoring growth for 28 h while aliquots, while taking aliquots at regular times for optical density measurements using a Ultrospec 2100 UV-Visible Spectrophotometer (Biochrom, UK).

Asymmetric reduction. The reactions were carried out in a 25-mL Erlenmeyer flask. The cells were suspended in 10 mL TRIS buffer (10 mM, pH 8.0) containing 1.0 mM acetophenone (substrate, Sigma-Aldrich, USA) and 60.0 mM isopropanol (co-substrate, Sigma-Aldrich, USA) then incubated on a reciprocal shaker at 180 rpm at 32 ^{o}C for 24 h. Aliquots (200 μL) were withdrawn at specified time intervals. For cell reusability characterization, the reaction was repeated over five batches (24 h per batch). For each batch, the cells were recovered by centrifugation, and then added again to a fresh batch of reaction medium to start a new batch of the reaction. Aliquots (200 μL) were withdrawn

at the beginning and the end of each batch. The product and the residual substrate were extracted with acetic ether (200 μL) containing 1.0 mM benzaldehyde (internal standard, Sigma-Aldrich, USA) prior to gas chromatography (GC) analysis.

GC analysis. This reaction was analyzed by a Perkin Elmer AutoSystem XL GC with a flame ionization detector and a chiral column (Elite Betacydex, 30 m × 0.25 mm × 0.25 μm, USA) with a split ratio of 20:1. The injector was kept at 240 °C, and the detector was kept at 230 °C. The column temperature was held at 80 °C for 2 min, increased from 80 °C to 150 °C at 5 °C/min, increased from 150 °C to 200 °C at 15 °C/min, and finally held at 200 °C for 5 min. Nitrogen was used as the carrier gas at a flow rate of 1.20 mL/ min. The retention-times for benzaldehyde, acetophenone, (*R*)-1-phenylethanol and (*S*)-1-phenylethanol were 8.2, 11.0, 12.4 and 12.6 min, respectively.

Post-functionalization on cells in PDA nanocoating. For titania functional layer introduction, cell@PDA was immersed in 10 mL TRIS buffer solution (pH 8.5, 10 mM), mixed with 100 μL TiBALDH (Sigma-Aldrich, USA) and shaken gently for 3 h. The result cells were washed with TRIS buffer (50 mM, pH 8.0) and collected by centrifugation. In order to characterize cell stability under UV light, native cell, cell@PDA, and cell@PDA@TiO_2 were irradiated under UV light for 4 h and subsequently carried on asymmetric reduction for 24 h. The

PDA-TiO_2 particles were synthesized through adding 100 μL TiBALDH (Sigma-Aldrich, USA) into a 10 mL PDA particle solution for 3 h shaking.

For silica functional layer introduction, cell@PDA was immersed in 10 mL TRIS buffer solution (pH 8.5, 10 mM) containing 10 mM *L*-lysine and shaken for 6h. Subsequently, the *L*-lysine modified cell@PDA was collected by centrifugation and mixed with TRIS buffer (50 mM, pH 8.0) of 5 mg/mL silica colloidal nanoparticles (LUDOX® HS-40, Sigma-Aldrich, USA) for 30 min. The result cells were washed with TRIS buffer (50 mM, pH 8.0) and collected by centrifugation. In order to characterize cell stability under heat condition, native cell, cell@PDA, and cell@PDA@TiO_2 were immersed into 45 ^oC water bath for 1 h and subsequently applied for asymmetric reduction for 24 h.

For magnetism functionalized, cell@PDA was immersed in 10 mL TRIS buffer solution (pH 8.5, 10 mM) of 0.5 mg/mL carboxylic acid functionalized iron oxide nanoparticles (Sigma-Aldrich, USA) for 3 h. The result cells were washed with TRIS buffer (50 mM, pH 8.0) and collected by centrifugation.

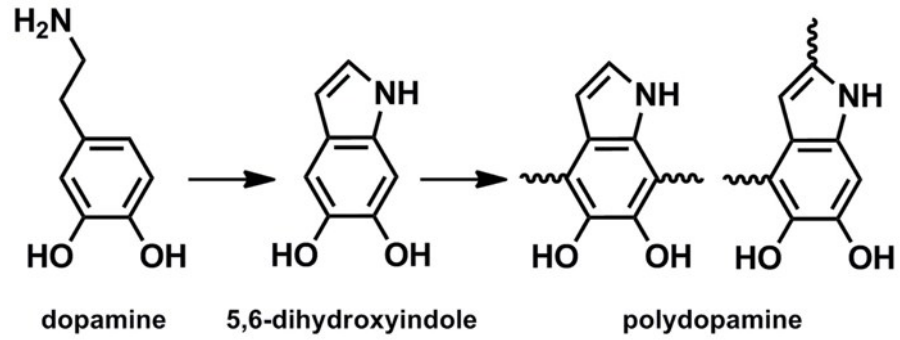

Figure S1. The pH-triggered oxidative polymerization mechanism of dopamine to PDA according to the literature.[14]

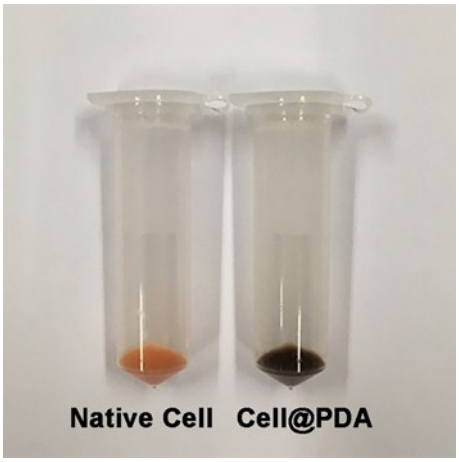

Figure S2. Optic image of the native cell and cell@PDA.

Table S1. The viability of the native cell, cell@PDA, cell@PDA@TiO_2, cell@PDA@SiO_2, cell@PDA@Fe_3O_4. Viability was expressed as the percentage live cells, visualized after LIVE/DEAD® Yeast Viability Kit staining and observed using CLSM. All experiments were carried out in three fold with separately cultured cells and data represent averages ± standard deviations obtained after counting a total of 200 cells for each experiment group.

Cell Group	Native Cell	Cell@PDA	Cell@PDA @TiO_2	Cell@PDA @SiO_2	Cell@PDA @Fe_3O_4
Viability	98 ± 1	95 ± 3	94 ± 3	94 ± 1	90 ± 2

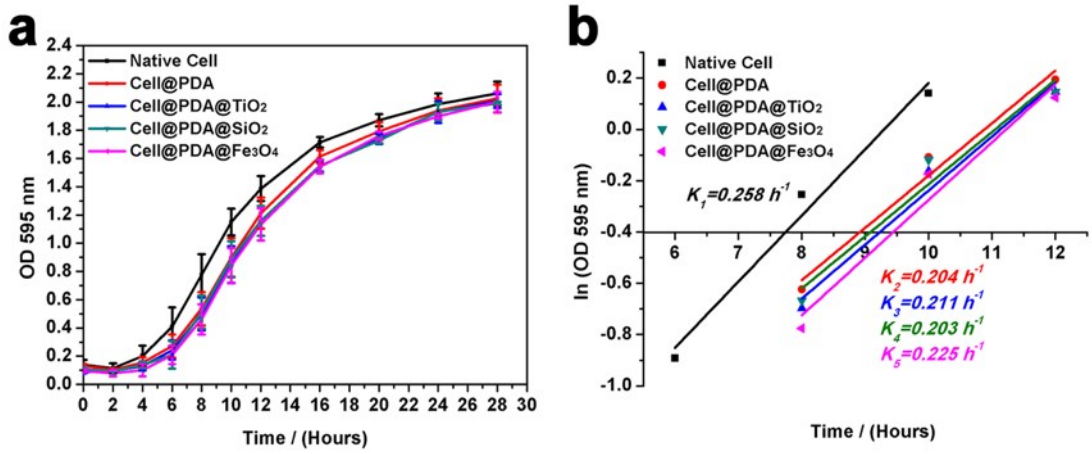

Figure S3. Optical densities at 595 nm of the native cell, cell@PDA, cell@PDA@TiO_2, cell@PDA@SiO_2, cell@PDA@Fe_3O_4 in growth medium as a function of time, plotted linearly (a) and logarithmically (b). Error bars indicate standard deviations over three independent cultures.

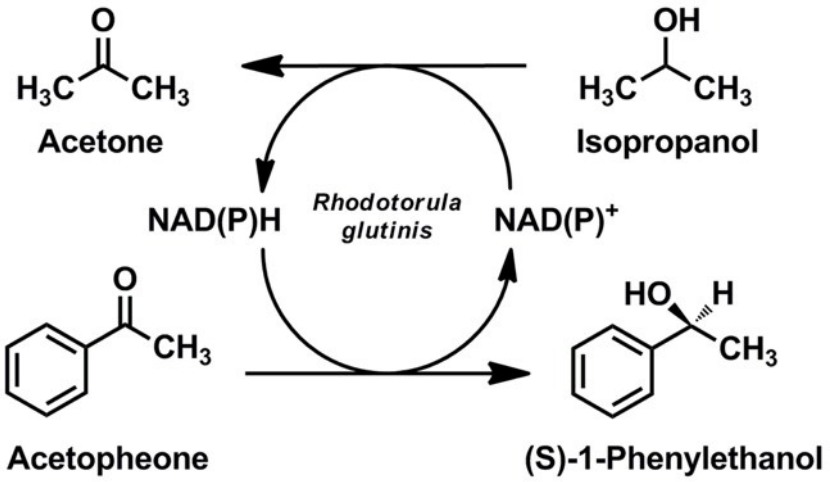

Figure S4. Schematic illustration of asymmetric reduction of acetopheone by *Rhodotorula glutinis*. Alcohol dehydrogenases in *Rhodotorula glutinis* can catalyze the reduction from acetophenone into (*S*)-1-phenylethanol, coupled with oxidation of internal cofactors (ß-1,4-nicotinamide adenine dinucleotide (NADH), ß-1,4-nicotinamide adenine dinucleotide phosphate (NADPH)). Isopropanol was simultaneously added as cosubstrate for driving the cofactors regeneration.

Table S2. Asymmetric Reduction of the native cell, cell@PDA and PDA. Error bars indicate standard deviations over three independent reactions.

Biocatalyst	Yield (%)	Reaction Time (h)	Product *e.e.* (%)	Productivity (mmol/L/h)
Native Cell	39.7 ± 0.5	24	>99.0	0.017
Cell@PDA	79.8* ± 2.0	9	>99.0	0.089
PDA	-	24	-	-

* Significantly different from the native cell at $p < 0.001$

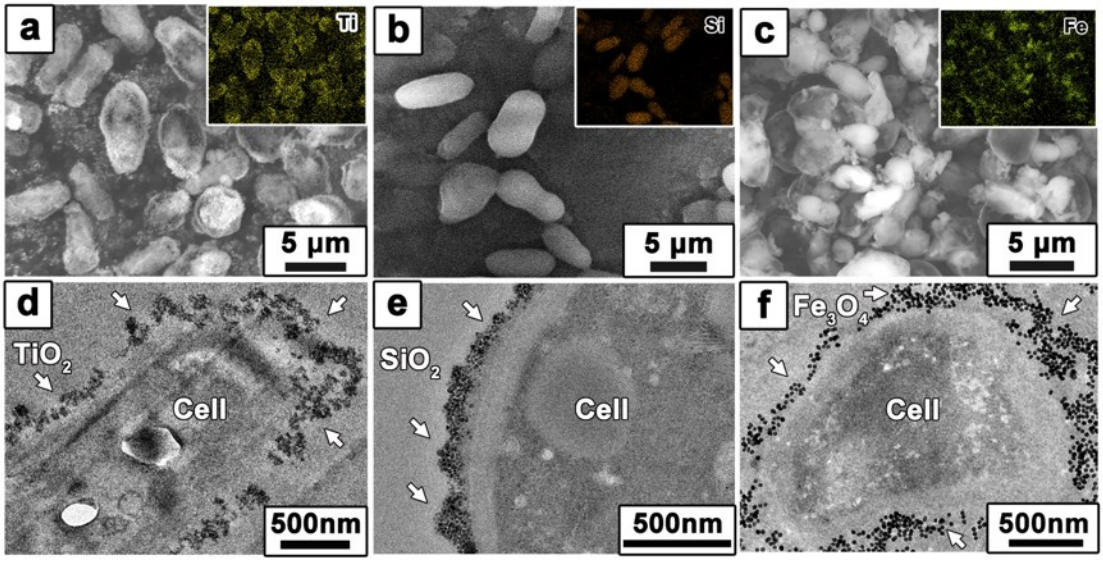

Figure S5. (a-c) SEM images of cell@PDA@TiO_2 (a), cell@PDA@SiO_2 (b), and cell@PDA@Fe_3O_4 (c), and the corresponding EDX mapping (insets), respectively. (d-f) TEM micrographs of cell@PDA@TiO_2 (d), cell@PDA@SiO_2 (e), and cell@PDA@Fe3O4 (f), respectively. The TiO_2, SiO_2 and Fe_3O_4 nanoparticles are indicated by arrows.

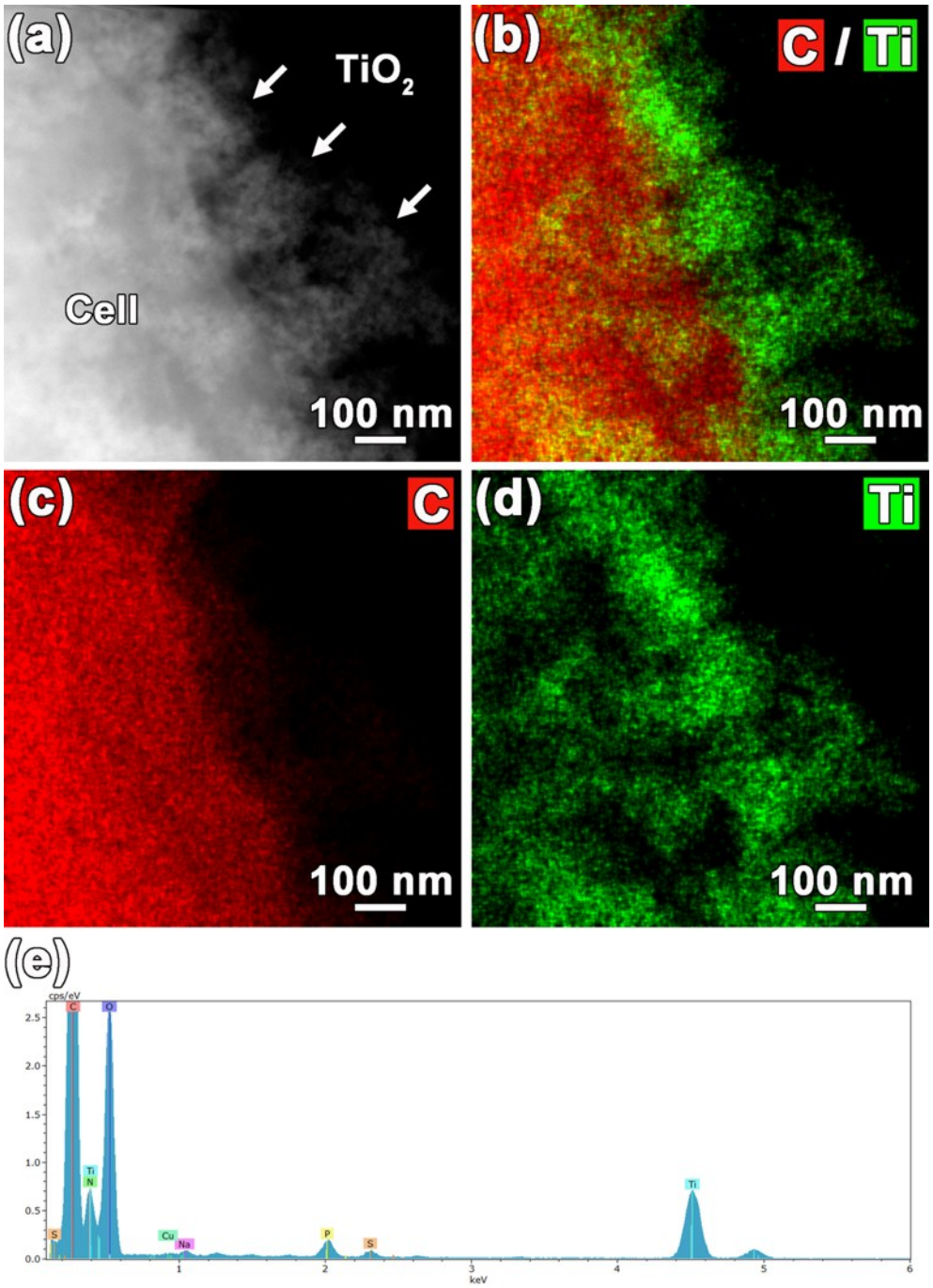

Figure S6. (a) High magnification HAADF-STEM image of cell@PDA@TiO_2 and the TiO_2 particles are indicated by arrows (b-d) Corresponding EDX elemental mapping results of the same area in (a), C: red, Ti: green. (e) Corresponding EDX spectrum.

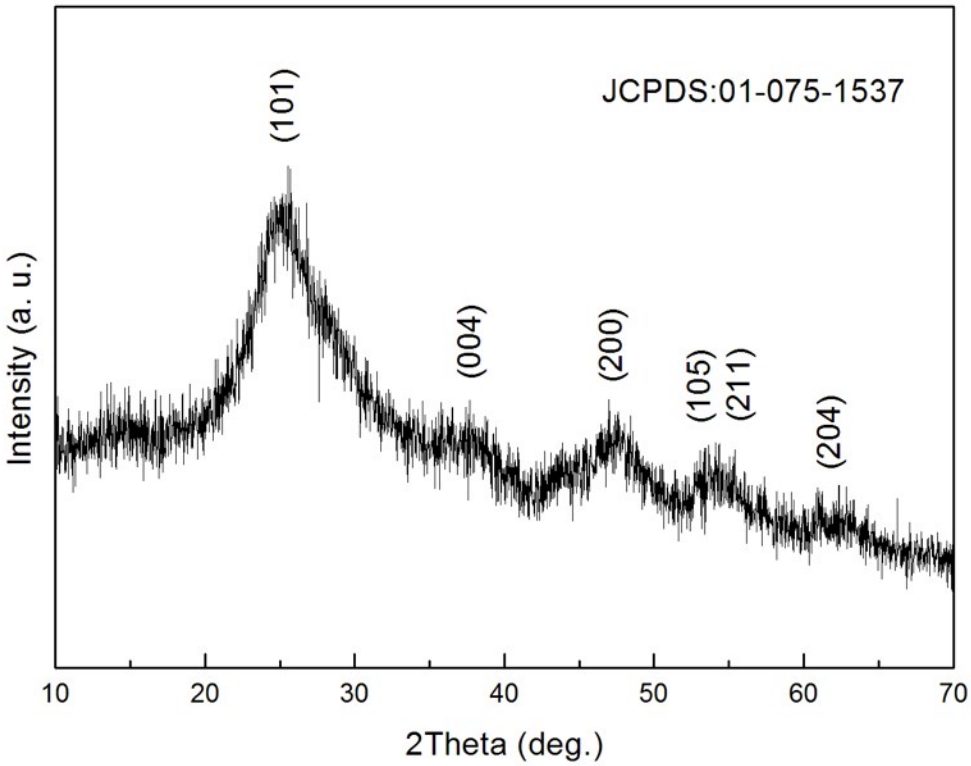

Figure S7. XRD pattern of the PDA-TiO_2 particles.

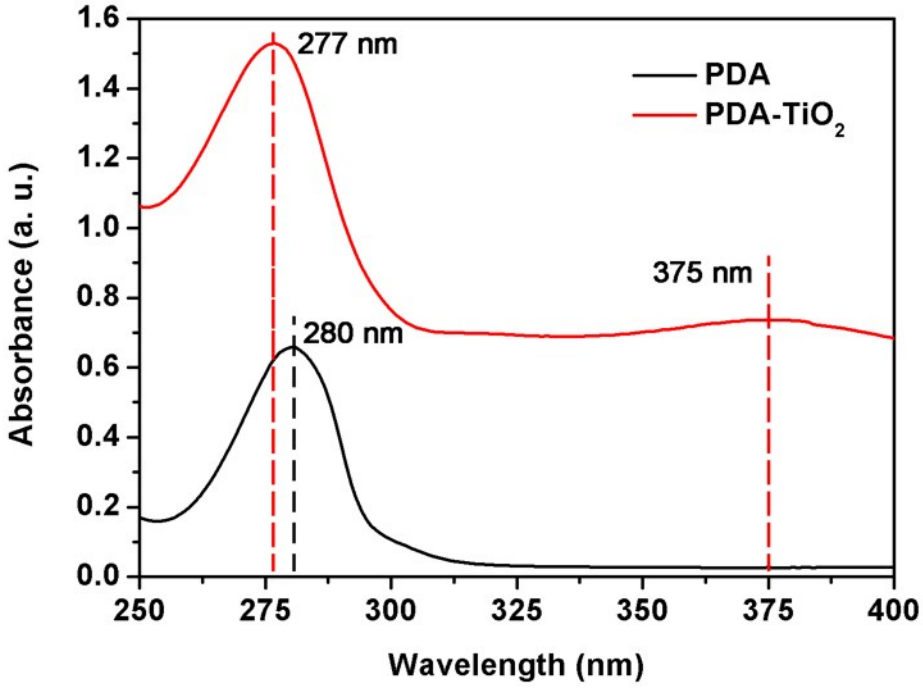

Figure S8. UV-visible spectra of the PDA particles and the PDA-TiO_2 particles.

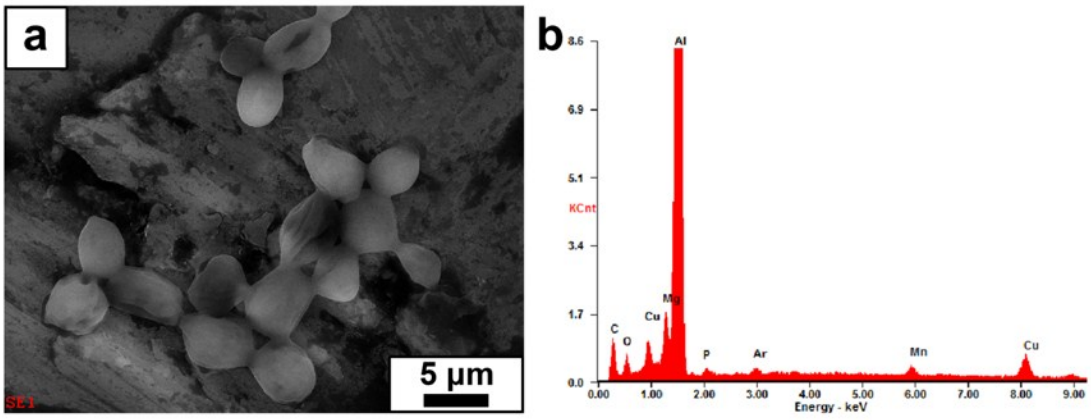

Figure S9. SEM image (a) of the native cells and the corresponding EDX spectrum (b).

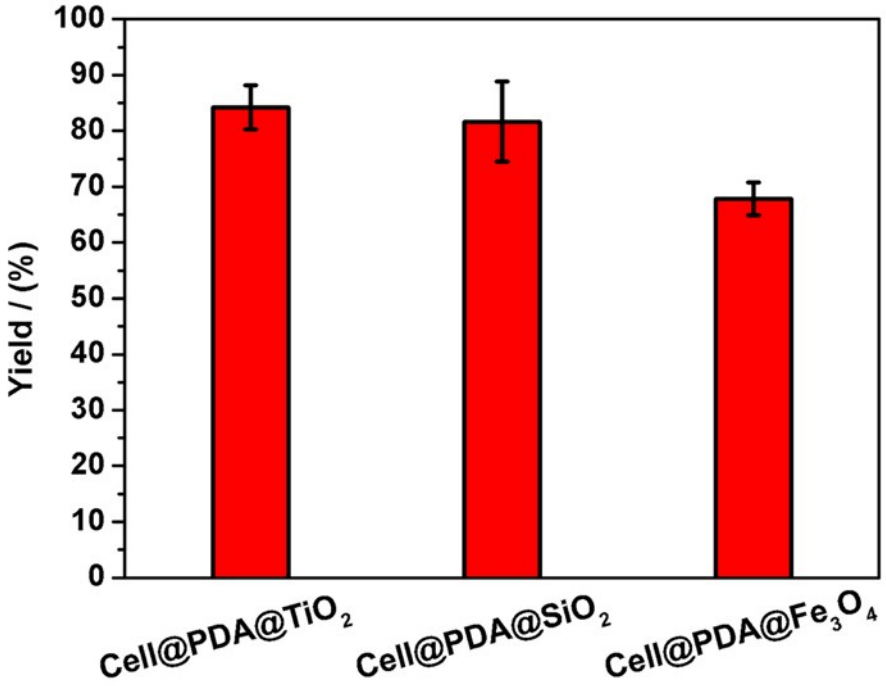

Figure S10. 24 h (*S*)-1-phenylethanol yield of cell@PDA@TiO_2, cell@PDA@SiO_2, and cell@PDA@Fe_3O_4. Error bars indicate standard deviations over three independent reactions.

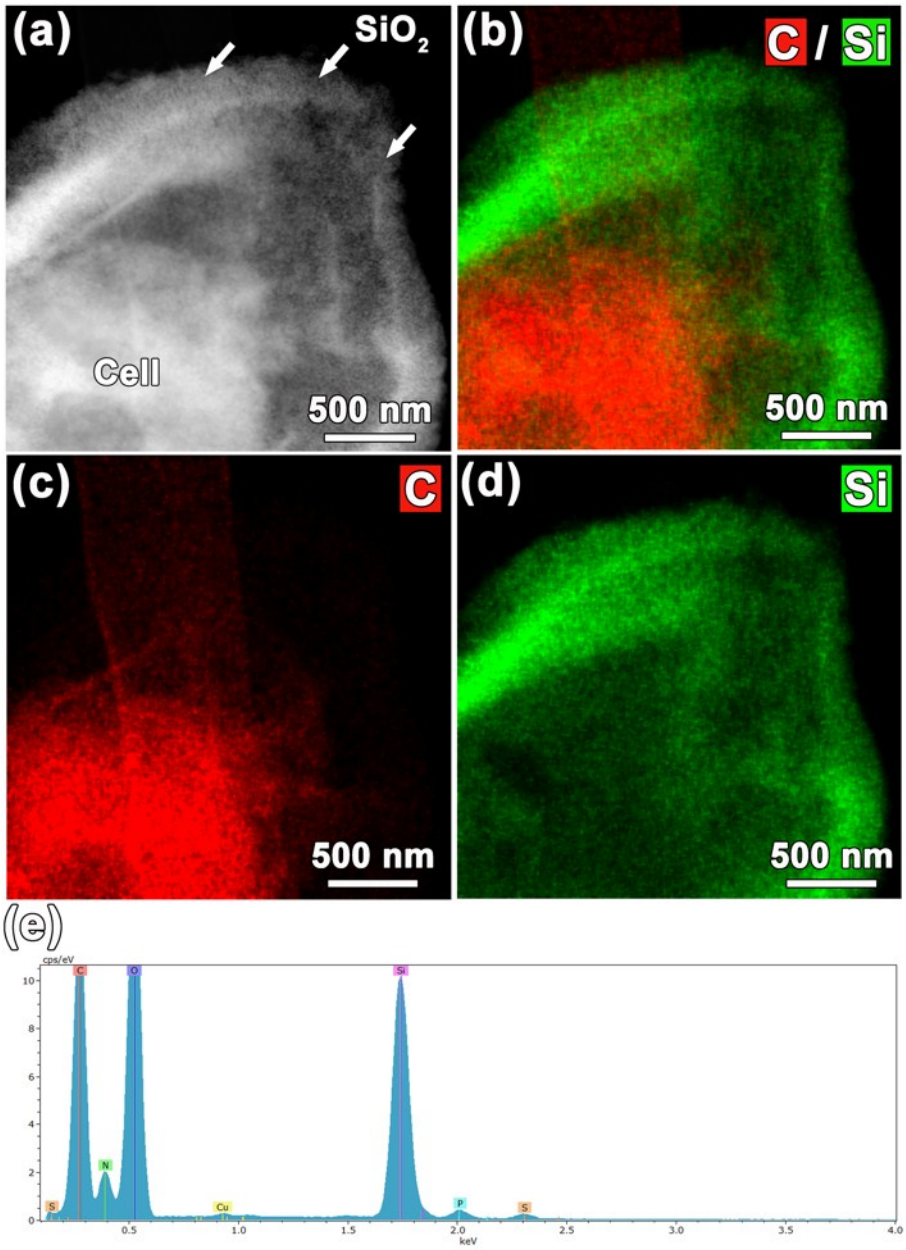

Figure S11. (a) High magnification HAADF-STEM image of cell@PDA@SiO_2 and the SiO_2 particles are indicated by arrows. (b-d) Corresponding EDX elemental mapping results of the same area in (a), C: red, Si: green. (e) Corresponding EDX spectrum.

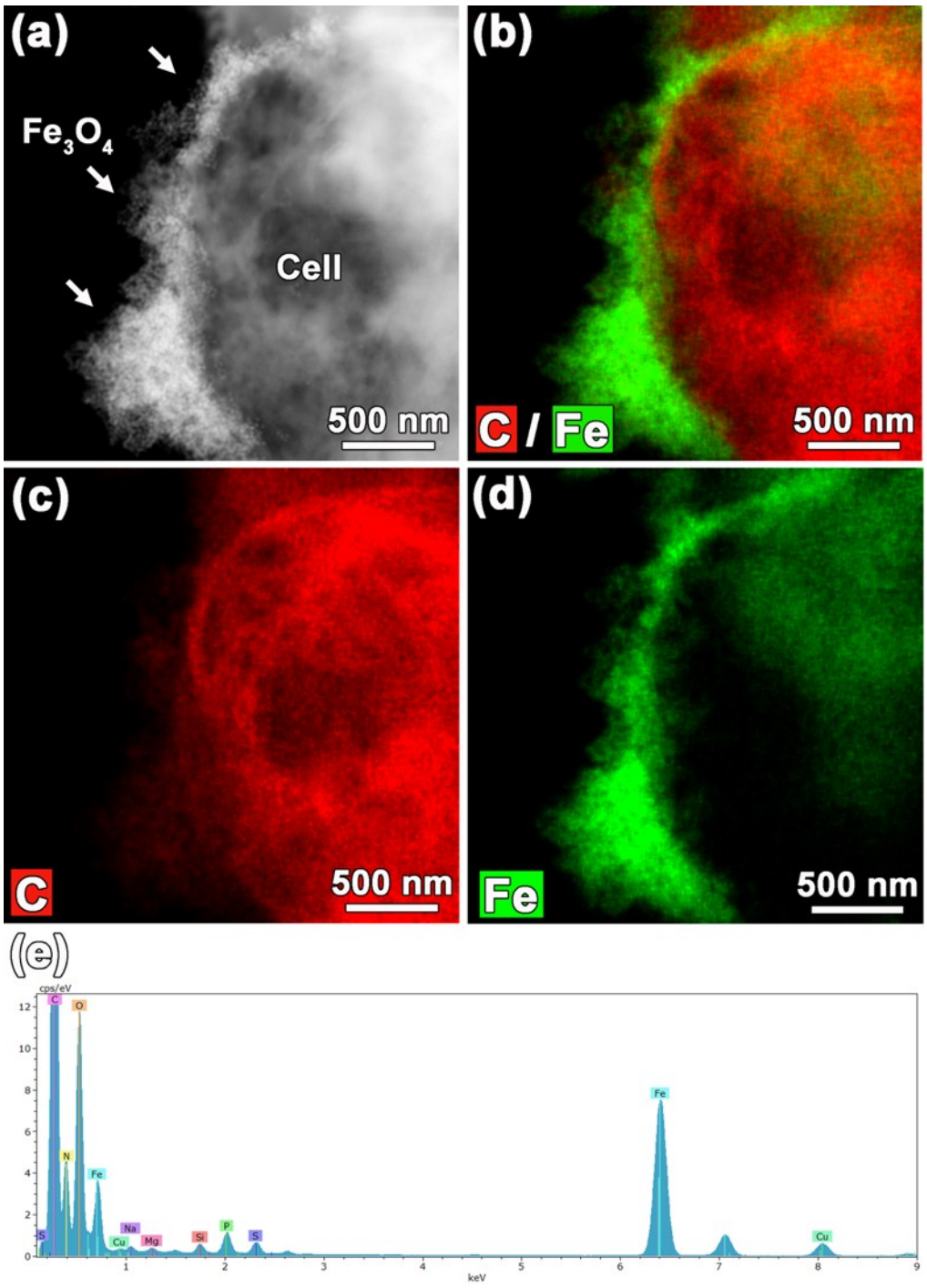

Figure S12. (a) High magnification HAADF-STEM image of cell@PDA@Fe_3O_4 and the Fe_3O_4 particles are indicated by arrows. (b-d) Corresponding EDX elemental mapping results of the same area in (a), C: red, Fe: green. (e) Corresponding EDX spectrum.

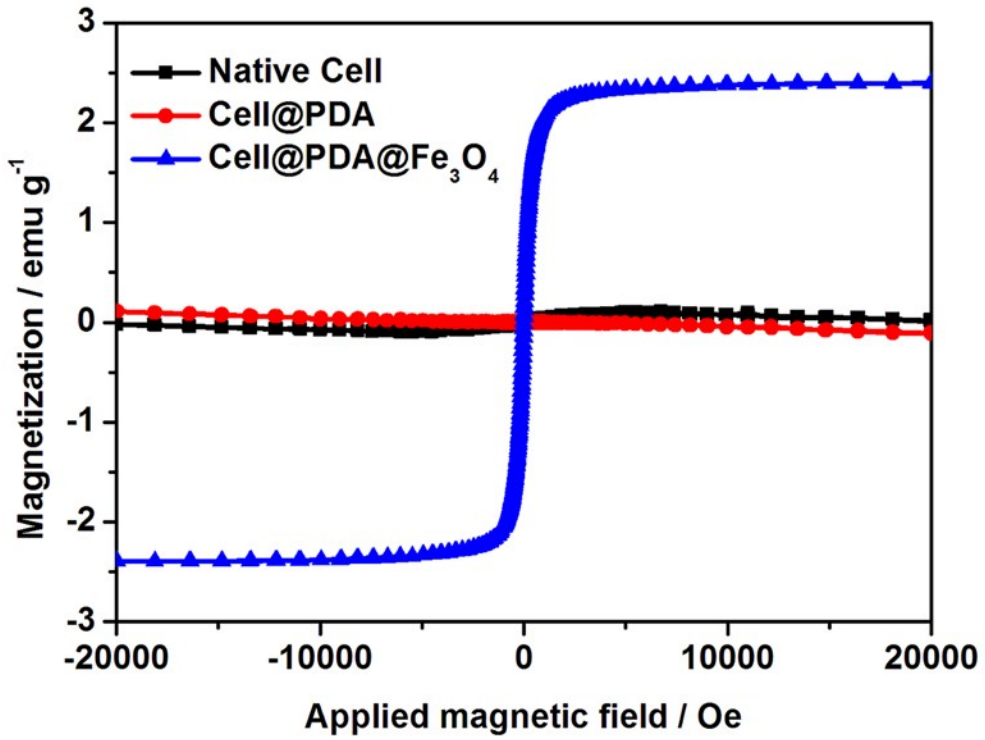

Figure S13. Magnetic hysteresis curves of the native cells, cell@PDA, and cell@PDA@Fe_3O_4 at 300 K.