Electronic Supplementary Information

Positional Immobilization of Pd Nanoparticles and Enzyme in Hierarchical Yolk-shell@shell Nanoreactors for Tandem Catalysis

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Experimental section

Table S1. Physicochemical parameters of MSN, NH2-MSN, Pd/NH2-MSN and Pd/NH2-MSN@BTME, NH2-MSN@BTME@L-mesosilica, NH2-MSN@BTME@enzyme/L-mesosilica and Pd/NH2-MSN@BTME@enzyme/L-mesosilica (after recycling)

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Fig. S2. The thermogravimetric analysis of NH2-MSN

Fig. S3. (a) and (b) TEM images of Pd/NH2-MSN with different magnifications, (c) STEM image of Pd/NH2-MSN, (d) statistic estimation of the Pd particle size

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Fig. S7. N2 sorption isotherms and pore size distribution curves of (a) NH2-MSN@BTME@L-mesosilica, (b) NH2-MSN@BTME@enzyme/L-mesosilica, (c) Pd/NH2-MSN@BTME@enzyme/L-mesosilica (after recycling)

Fig. S8. Schematic reaction flow of the cascade reaction sequences on the yolk–shell@shell structured bifunctional catalyst

Experimental section
Chemicals and materials

All chemicals were used as received unless otherwise stated. Tetraethylorthosilicate (TEOS, AR), ammonia solution (25-28%), cetyltrimethyl ammonium bromide (CTAB), cetyltrimethyl ammonium chloride (CTAC) and triethanolamine (TEA) were purchased from Shanghai Chemical Reagent Company of the Chinese Medicine Group. 1,2-bis(trimethoxysilyl)ethane (BTME) was obtained from Sigma-Aldrich. Li2PdCl4 was purchased from Aladdin-reagent Company. 3-aminopropyltrimethoxysilane (APTMS) was purchased from J&K Scientific. Native Lipase B from Candida Antarctica (CALB) was purchased from Novozymes.

Synthesis of mesoporous silica nanospheres (MSN)

The mesoporous silica nanospheres was synthesized through a sol-gel process of TEOS in the presence of CTAB as template reagent. 0.40 g of CTAB was dissolved into the mixture of 192 ml H2O and 1.4 ml NaOH solution (2 M) at 80 °C. After stirring for 15 min, 2.40 g of TEOS was added and stirred for 2 h. After cooling to room temperature, the powder product was isolated by filtration, washed with ethanol and air-dried. To remove the surfactant, the as-synthesized materials (1 g) were dispersed in a solution of 80 mg ammonium nitrate and 120 ml ethanol (95%) solution. The mixture was heated at 60 °C for 20 min and the process was repeated for three times.

Synthesis of amino-functionalized MSN through post-grafting method (NH2-MSN)

0.50 g of dry MSN and 1.0 ml of 3-aminopropyltrimethoxysilane were added into 30 ml of toluene, and the mixture was refluxed for 24 h under argon. After filtration, the white solid was washed with toluene and ethanol, dried at 60 °C in vacuo for 24 h to give the NH2-MSN.

Preparation of Pd/NH2-MSN

To a suspension of NH2-MSN (0.50 g, 2.86 mmol/g -NH2) in deionized H2O (20 ml) was added Li2PdCl4 (61.6 mg, 0.235 mmol) in deionized H2O (5 ml). After stirring at room temperature for 24 h, the solid was separated by centrifugation and washed with deionized H2O. Then, the solid material was re-dispersed into 20 ml of water, and NaBH4 aqueous solution (2.35 mmol, 1M) was added drop-by-drop for reduction about 30 min. The Pd/NH2-MSN was isolated by centrifugation and washed with deionized H2O and ethanol.

Synthesis of yolk-shell nanospheres (Pd/NH2-MSN@BTME)

Pd/NH2-MSN as core material (80 mg) was dispersed into 20 ml water by sonication, Then, deionized water (40 ml), ethanol (20 ml), CTAB (0.15 g) and NH3·H2O (0.5 ml, 25 wt%) were added successively at 38 °C. After stirring for 15 min, 0.25 ml of TEOS dissolving in ethanol (2 ml) was added and stirred for 2 h. Then, the temperature was heated to 45 °C, and a mixture of FC4 (0.02 g), CTAB (0.04 g), NH3·H2O (0.1 ml), 1.5 ml
H₂O was added. After stirring for 15 min, BTME solution (0.18 ml BTME, 2.0 ml ethanol) was added and stirred for 2 h. Then, the temperature was heated to 80 °C and etched for 1.5 h. The powder product was collected by filtration and dried at room temperature.

Fabrication of yolk-shell@shell nanospheres (Pd/NH₂-MSN@BTME@L-mesosilica)

The dendrimer-like outer shell with large pore size was achieved via a one-pot bi-phase stratification approach using cationic surfactant CTAC as a template, TEOS as a silica source, TEA as a catalyst. At first, 3.0 g of CTAC was dissolved into 30 ml of water at 60 °C. Then, 0.09 g of TEA and 250 mg Pd/NH₂-MSN@BTME of were added and ultrasonic treated for 30 min. After stirring at 60 °C for 1 h, 10 ml of (10 v/v %) TEOS in cyclohexane was carefully added to the water-CTAC-TEA solution and kept at 60 °C in an oil bath under a magnetic stirring for about 12 h. The final product was collected by filtration and washed with ethanol for several times. The Pd loading was determined to be about 1.14 wt% by ICP.

Immobilization of CALB into Pd/NH₂-MSN@BTME@L-mesosilica nanoreactors

Pd/NH₂-MSN@BTME@L-mesosilica (250 mg) was stirred overnight in potassium phosphate buffer (pH = 8.0) with a 9.0 mg/ml solution of CALB (3.0 ml). The resulting product was centrifuged, washed several times with potassium phosphate buffer and dried at room temperature under vacuum. The amount of CALB that had been accommodated inside the solid support was calculated from the difference in concentration of the lipase solution before and after immobilization. And the immobilized amount of CALB was calculated to be 35 mg/g. Also, the Pd loading content of final cascade reactor was determined by ICP characterization to be 1.08 wt%.

For the synthesis of control sample NH₂-MSN@BTME@enzyme/L-mesosilica, the procedures were similar except that NH₂-MSN without Pd nanoparticles was used as the core material. The immobilized amount of CALB was calculated to be 32 mg/g.

Characterization

Nitrogen sorption experiments were carried out on micrometritics ASAP2020 volumetric adsorption analyzer. Before the measurements, samples were degassed at 373 K for 6 h. The BET surface area was evaluated from the adsorption data in the relative pressure P/P₀ range from 0.04 to 0.2. The total pore volume was estimated from the amount adsorbed at the P/P₀ value of 0.99. Pore size distributions were determined from the adsorption branches using a BJH method. Transmission electron microscopy (TEM) was performed on a HITACHI 7700 microscope at an acceleration voltage of 100 kV. Thermogravimetric analysis (TGA) was performed under an air atmosphere with a heating rate of 5 °C/min by using a NETZSCH
STA-449F3 thermogravimetric analyzer. Scanning electron microscope (SEM) images were performed using a Hitachi SU 1510. XRD patterns were recorded on a Rigaku RINT D/Max-2500 powder diffraction system by using CuKα radiation.

**Adsorption tests of Pd/NH₂-MSN@BTME@L-mesosilica and Pd/NH₂-MSN@BTME**

For the comparison of different adsorption ability of Pd/NH₂-MSN@BTME@L-mesosilica and Pd/NH₂-MSN@BTME, the typical procedure was as follow: solid material (20 mg) was suspended into 3 ml of CALB potassium phosphate buffer solution (0.10 mg/ml) and stirred at room temperature for desired time. After centrifugation, the supernatant was detected using UV-Vis, and the adsorption amount was calculated.

**Procedure of racemization and dynamic kinetic resolution of 1-phenylethylamine**

Typically, 1-phenylethylamine (0.50 mmol), ethylmethoxy acetate (1.00 mmol), Na₂CO₃ (40 mg) and solid catalyst Pd/NH₂-MSN@BTME@enzyme/L-mesosilica (150 mg) were added into a 10-ml Schlenk tube with 3.0 ml of toluene as solvent. After air exhaust by evacuating, the reaction was performed under stirring at 70 °C with a 5 L hydrogen balloon. After a high-speed centrifugation, the supernatant liquor was used to monitor the conversion, enantiomeric excess and selectivity on an Agilent 7890 gas chromatograph with a Supelco-β-DEX TM 225 chiral column (0.25 mm × 30 m × 0.25 µm). For the recycling tests, the solid catalyst was centrifuged after reaction, and another portion of reactants were added directly for the next running. The Pd loading of the reused nanoreactors was determined to be 1.12 wt%.
<table>
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<tr>
<th>sample</th>
<th>BET surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore size (nm)</th>
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<tr>
<td>MSN</td>
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<tr>
<td>NH₂-MSN</td>
<td>740</td>
<td>0.629</td>
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<td>0.485</td>
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<td>0.785</td>
<td>2.3, 7.2</td>
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<td>NH₂-MSN@BTME@enzyme/L-mesosilica</td>
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<td>0.433</td>
<td>6.2</td>
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<td>Pd/NH₂-MSN@BTME@enzyme/L-mesosilica (after recycling)</td>
<td>403</td>
<td>0.672</td>
<td>7.1</td>
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</tbody>
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