Electronic Supplementary Information

Fe₃O₄-Au@mesoporous SiO₂ microsphere: an ideal artificial enzymatic cascade system

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Experimental Section

Chemicals. FeCl₃⁻⁶H₂O, trisodium citrate, sodium acetate (NaAc), acetic acid, ethylene glycol, tetraethyl orthosilicate (TEOS), cetyltrimethylammonium bromide (CTAB), HAuCl₄⁻⁴H₂O, H₂O₂, acetone, ethanol, concentrated ammonia solution (28 wt %) and NaBH₄ were of analytical grade and purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. D-(+)-glucose and 3,3,5,5-tetramethylbenzidine (TMB) were obtained from Sigma-Aldrich. Deionized water was used for all experiments.

Synthesis of Fe_3O_4 -Au particles. Fe_3O_4 particles were obtained via a method described in the literature with minor modification.¹ Typically, 0.70 g FeCl₃'6H₂O, 0.28 g trisodium citrate were first dissolved in 20 mL ethylene glycol, and then 1.20 g NaAc was added to the above solution with stirring until the mixture was uniform. The obtained yellow solution was sealed in an autoclave. The autoclave was heated at 200 °C for 10 h, and then allowed to cool to room temperature. The products were washed with ethanol and water for several times. 40 mg prepared Fe_3O_4 particles were dispersed in 50 mL nitrogen-saturated water by sonication for 5 min. Subsequently, 0.5 ml of HAuCl₄'4H₂O (1.62%) solution was added to above dispersion, and then mechanically stirred for 30 min. A freshly prepared NaBH₄ (2 mL; 0.15 M) was added into the above mixture under vigorous stirring. After the resulted suspension was stirred for another 0.5 h, the solution containing Fe_3O_4 -Au particles was obtained. With the help of a magnet, the microspheres were separated, and washed with nitrogen-saturated water for 3 times.

Synthesis of Fe_3O_4 -Au@mesoporous SiO₂ microspheres. To enhance the stability of the obtained Fe_3O_4 -Au particles, a mesoporous silica shell was introduced according a reported method.² Fe₃O₄-Au particles (100 mg) were added into a mixed solution containing CTAB (40

mg), deionized water (25 mL), concentrated ammonia solution (0.5 mL), and ethanol (37 mL). After the mixed solution was ultrasonicated for 20 min, 120 μ L of TEOS was added dropwise to the dispersion under vigorous stirring. After continuous stirring for 8h at room temperature, the product was washed with ethanol and water for several times. The resulting products were subjected to a Soxhlet extraction with acetone for 2 days to remove the CTAB. Finally, the products were washed with deionized water, and Fe₃O₄-Au@MS composite microspheres were obtained.

Construction of the artificial enzymatic cascade system. Firstly, we investigated the peroxidase-mimic activity of Fe_3O_4 -Au@MS microspheres. The peroxidase-mimic catalytic reactions were carried out at room temperature in a 4 ml tube with 0.1 mg Fe_3O_4 -Au@MS in 2 ml of reaction buffer in the presence of a certain amount of H_2O_2 , using 0.02 mg TMB as the substrate. The construction of the artificial enzymatic cascade system was performed as above experiment using glucose instead of H_2O_2 . After the reaction proceeded for a certain time, Fe_3O_4 -Au@MS composite microspheres were removed from the reaction solution by an external magnetic field. All the resulting solutions were used for absorbance measurement at a wavelength of 652 nm.

Characterization. The particles were sputtered with Au in order to observe the morphology using a Hitachi S-4300 Scanning Electron Field Emission Microscope (SEM). Transmission electron microscope (TEM) images were obtained with a JEM-2100 electron microscope operating at 200 kV. UV-vis absorbance spectra were recorded using a JASCO V-570 spectrophotometer at room temperature. X-ray-powder diffraction patterns were accumulated on a Japan Rigaku D/max γ A X-ray diffractometer by using graphite monochromatised Cu_{Ka} radiation (λ =1.5418 Å). Nitrogen

adsorption-desorption measurements were carried out on a Quadra-Sorb SI automated surface area

and pore-size analyser at -196° C by using the volumetric method.

Notes and references.

1. J. Liu, Z. Sun, Y. Deng, Y. Zou, C. Li, X. Guo, L. Xiong, Y. Gao, F. Li and D. Zhao, Angew.

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2. Z. Chen, Z. M. Cui, F. Niu, L. Jiang and W. G. Song, Chem. Commun., 2010, 46, 6524-6526.



Fig. S1 (a) SEM image of Fe_3O_4 particles, (b) SEM image at higher magnification, (c) TEM image of Fe_3O_4 particles, (d) TEM image at higher magnification.



Fig. S2 The FT-IR spectrum of the Fe_3O_4 particles. The bands at 580 and 430 cm⁻¹ are associated with the Fe-O stretching. The bands at 1068 and 3400 cm⁻¹ are ascribed to the C-H vibrating and O-H vibrating, respectively. Typical bands assigned to carboxylate group are visible at 1652 and 1396 cm⁻¹. This FT-IR spectrum indicates that Fe₃O₄ particles are capped with citrate groups.



Fig. S3 The wide-angle XRD patterns of (1) Fe_3O_4 particles, (2) Fe_3O_4 -Au particles, (3) Fe_3O_4 -Au@MS microspheres.



Fig. S4 The energy dispersive spectra of Fe₃O₄-Au particles



Fig. S5 (a) The pore size distribution of Fe_3O_4 -Au@MS microspheres, (b) the nitrogen adsorption-desorption isotherms of Fe_3O_4 -Au@MS microspheres.

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Fig. S6 The magnetic hysteresis loops of the Fe_3O_4 particles (black), the Fe_3O_4 -Au particles (red), and the Fe_3O_4 -Au@MS microspheres (green). Inset: images of solution before (a) and after (b) magnetic separation of Fe_3O_4 -Au@MS microspheres.



Fig. S7 The photograph of the color change of different samples after magnetic separation of Fe_3O_4 -Au@MS microspheres. (a) TMB; (b) TMB/H₂O₂ (200µM, t=10 min); (c) TMB/glucose (500µM, t=30 min); (d) TMB/Fe₃O₄-Au@MS microspheres; (e) TMB/Fe₃O₄-Au@MS microspheres /H₂O₂ (200µM, t=10 min); (f) TMB/Fe₃O₄-Au@MS microspheres/glucose (400µM, t=30 min).



Figure S8 The effect of pH on the catalytic activity of the artificial enzymatic cascade system based on Fe_3O_4 -Au@MS microspheres. Glucose was 500 μ M.



Fig. S9 Glucose concentration response curves (pH=4.0; reaction time was 30 min). Glucose concentrations are 0.5 μ M and 0 μ M respectively.

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Fig. S10 (a) Absorbance of reaction mixture (Fe3O4-Au@MS/glucose/TMB) changing with reaction time proceeding. (b) Absorbance of reaction mixture (Au&Fe3O4 NPs/ glucose/ TMB) changing with reaction time proceeding. (c) Reaction rate comparison of Fe3O4-Au@MS/glucose/TMB and Au&Fe3O4 NPs/glucose/TMB. (d) The reusability of Fe3O4-Au@MS microspheres and Au&Fe3O4 NPs. Glucose is 500 µM (pH=4.0); Au nanoparticles we used are prepared by using HCl (0.5 M) to etch Fe3O4 away from the same amount of Au-Fe3O4 particles.

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Fig. S11 (a) TEM image of Fe_3O_4 -Au@MS microspheres after 6 successive artificial enzymatic cascade reactions, (b) TEM image of Fe_3O_4 -Au particles after 1 artificial enzymatic cascade reaction.