Electronic Supplementary Information

Spindle-shaped nanoscale yolk/shell magnetic stirring bars for heterogeneous catalysis in macro- and microscopic systems

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Materials: (1-hexadecyl)trimethyl ammonium bromide (CTAB), Tetraethoxysilane (TEOS) and Pd/C (5 wt%) were produced by Alfa Aesar. Styrene (extra pure) was provided by Acros. 4-chlorostyrene (98%, stabilized with 0.1% 4-tert-butylcatechol), 4-methoxystyrene (95%, stabilized), 2-vinylnaphthalene (98%), cyclohexene (99%) , 4-methylstyrene (98+%, stab. with 0.1% 3,5-di-tert-butylcatechol), and 1,3,5-trimethylbenzene (98%) was purchased from J&K scientific Co., Ltd. Methylene blue (MB), $FeCl_3\cdot6H_2O$ (A.R.), $NaH_2PO_4\cdot2H_2O$ (A.R.) and polyvinylpyrrolidone (PVP K-30, A.R.) were provided by Beijing Chemical Reagent Company.

Experimental Section:

Synthesis of α-Fe_2O_3 nanospindles: In a typical experiment, $FeCl_3\cdot6H_2O$ (0.405 g, 1.5 mmol) was dissolved in 75 mL 0.45 mmol/L NaH_2PO4 solution, then the obtained orange solution was transferred to a 100mL teflon autoclave, and heated at 105 °C in an electric oven for 48 h.

Synthesis of α-Fe_2O_3@SiO_2 nanospindles: The above synthesized α-Fe_2O_3 nanospindles were dispersed into a 60 mL solution containing CTAB (0.14 g), PVP K-30 (0.45 g), water (5 mL), and ethanol (55 mL) with the assitant of ultrasonic. The obtained suspension was stirred at room temperature using a magnetic stir bar, then a solution of TEOS (140 μL) in 15 mL ethanol was added dropwise, followed by 2 mL of $NH_3\cdot H_2O$. After 9 h, the reaction mixture was filtrated through a PTFE membrane with 0.2 μm pore diameter. The composites were washed with 50 mL H_2O for two times, and then washed with 50 mL ethanol. Finally, the obtained solid was dried in vacuum at room temperature for 8 h.

Synthesis of Fe@meso-SiO$_2$ yolk/shell nanostructures: Firstly, the above obtained α-Fe$_2$O$_3$@SiO$_2$ product was calcined at 500°C with heating rate of 2 °C/min for 1h in a tubular furnace under argon condition, then the argon flow was changed to air atmosphere for 1.5 h to remove CTAB template. After that, the air flow was changed to argon atmosphere for 0.5 h to exclude air in the tubular furnace. Finally pure H$_2$ was introduced to reduce α-Fe$_2$O$_3$ to metallic Fe at 500°C for 6 h. After cooling to room temperature, black powder was obtained.

Synthesis of Pd-Fe@meso-SiO$_2$ yolk/shell nanoreactors: In a 10 mL plastic tube, 10 mg Fe@*meso*-SiO$_2$ was dispersed into 9 mL water with magnetic stirring at room temperature. Then 50 uL NaPd$_2$Cl$_4$ (0.0564 mol/L) was added into the solution dropwise. After stirring for 9 h, the prepared Pd-Fe@*meso*-SiO$_2$ was washed with distilled water and ethanol three times and collected by the outer magnet. Finally, the precipitate was dried in vacuum at room temperature for 12 h.

The catalytic activity test of Pd-Fe@meso-SiO$_2$ (2.7 wt% Pd loading) for styrene hydrogenation reaction: A 25 mL steel autoclave was charged with catalyst (5.0 mg), styrene (285 μL, 2.5 mmol), 1,3,5-trimethylbenzene (internal standard, 285 μL, 2.0 mmol) and 5 mL ethanol. The autoclave was evacuated and backfilled with H$_2$ (3 cycles, 1.0 MPa). Then, the mixture was stirred in a 25 ^{o}C water bath under 1.0 MPa H$_2$ atmosphere for desired time. The product was analyzed by a gas chromatograph (Shimadzu GC-2010) equipped with a flame ionization detector (FID) and a Rtx-5 capillary column (0.25 mm in diameter, 30 m in length). The identity was ascertained by GC-MS (Shimadzu GCMS-QP2010S).

Synthesis of control sample loading Pd nanoparticles outside the silica shell: In a 50 mL plastic tube, 20 mg Fe@*meso*-SiO$_2$ was dispersed into 20 mL ethanol with magnetic stirring at room temperature, then 130 uL NaPd$_2$Cl$_4$ (0.0564 mol/L) was added into the solution. The reaction solution was stirred for 30 min after 100 uL hydrazine hydrate (85 wt%) was added immediately. Finally, the solid was recovered by by outer magnet and washed with distilled water and ethanol and dried under vacuum at room temperature for 12 h.

Hydrogenation reaction of methylene blue (MB) in tiny water drops: 50 μL MB solution (5x10^{-5} mol/L) was dripped onto a hydrophobic polytetrafluoroethylene (PTFE) plate. After 50 μL solution that contains Pd-Fe@*meso*-SiO$_2$ was added, the magnetic stirrer was turned on and began to count the time. The Pd-Fe@*meso*-SiO$_2$ containing solution was prepared by dispersing 3.0 mg Pd-Fe@*meso*-SiO$_2$ and 31.0 mg NaBH$_4$ in 9 mL H$_2$O and was used immediately.

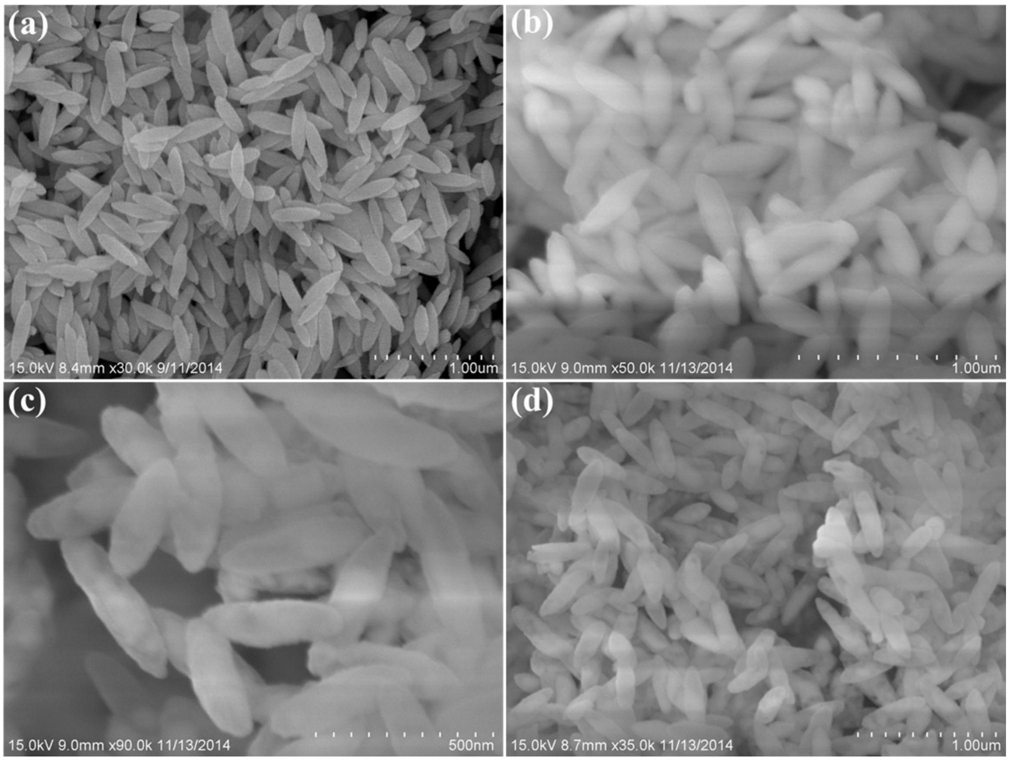


Fig. S1 SEM images of the obtained α-Fe_2O_3 nanospindles (a), α-Fe_2O_3@SiO_2 (b), Fe@*meso*-SiO_2 (c) and Pd-Fe@*meso*-SiO_2 (d).

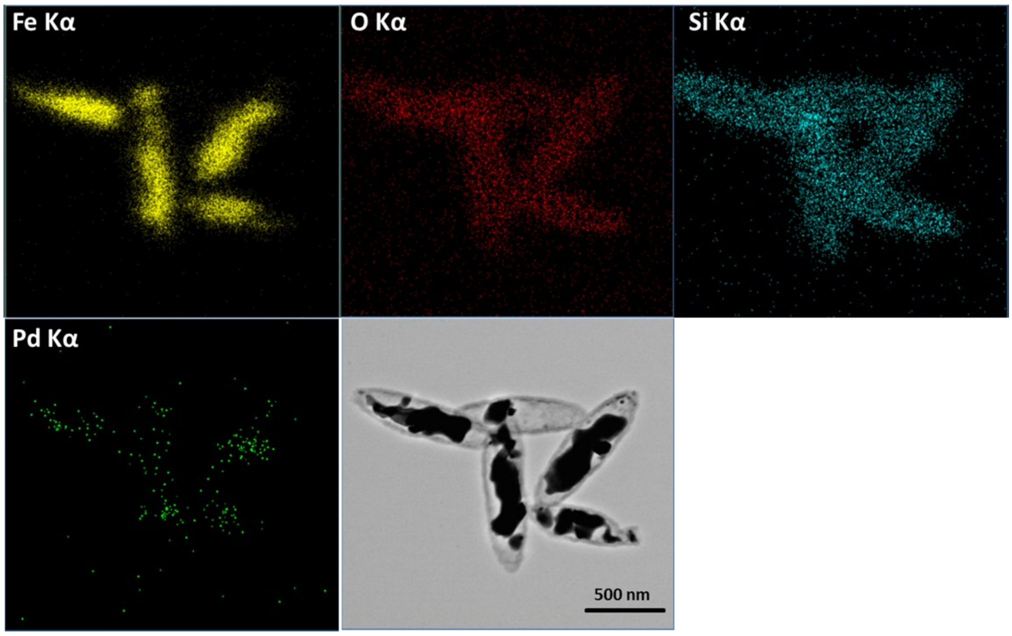


Fig. S2 Elements mapping of the Pd-Fe@*meso*-SiO_2 nanostructures.

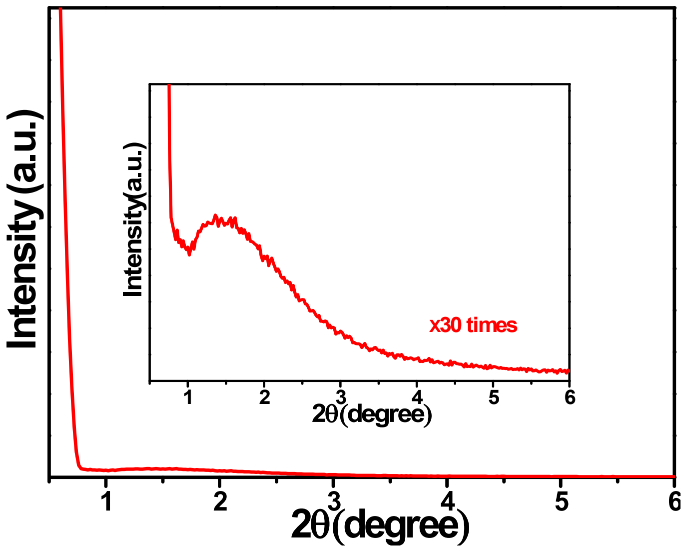


Fig. S3 Small-angle XRD pattern of the Pd-Fe@*meso*-SiO$_2$ nanostructures.

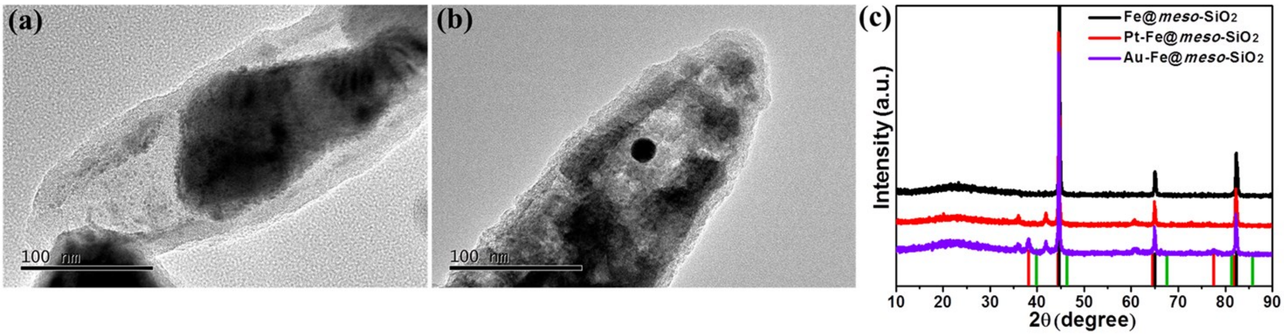
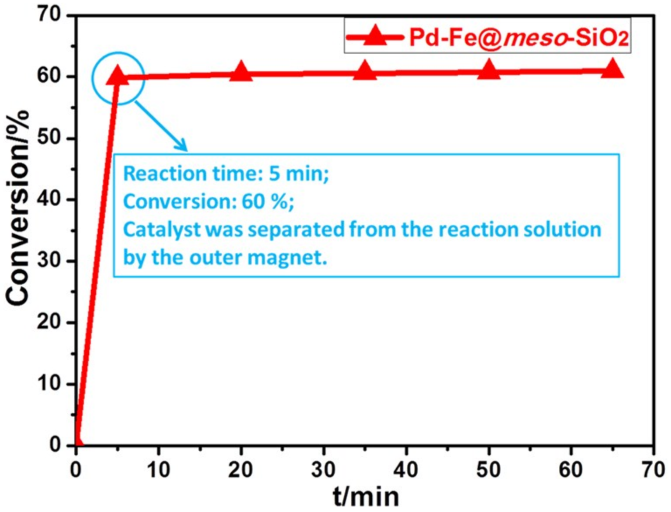


Fig. S4 TEM images of the Pt-Fe@*meso*-SiO$_2$ with 0.7 wt % Pt loading (a) and Au-Fe@*meso*-SiO$_2$ with 3.5 wt % Au loading (b). From the TEM images, it can be found that noble metal nanoparticles stayed inside the shell. XRD patterns (c) show no XRD diffraction peaks of Pt were found, which should be the small size of Pt NPs and the relative low Pt loading. Dark lines, green lines and red lines at the bottom were the standard Fe PDF card (JCPDS No. 06-0696), Pt PDF (JCPDS No. 87-0646) and Au PDF (JCPDS No. 65-2870), respectively.



Reaction time: 5 min;
Conversion: 60 %;
Catalyst was separated from the reaction solution by the outer magnet.

Fig. S5 Hot extraction experiments of catalyst Pd-Fe@*meso*-SiO$_2$. Reaction conditions: Pd-Fe@*meso*-SiO$_2$ (5.0 mg), 285 μL (2.5 mmol) styrene, 285 μL 1,3,5-trimethylbenzene as the internal standard, 5 mL ethanol, 1.0 MPa H$_2$, 25 ^{o}C. Catalyst was separated from the reaction solution at 5 min by the outside magnet. It can be seen that no further conversion of styrene was detected even the reaction time was prolonged to 65 min. This result showed that the catalysis process was exclusively heterogeneous.

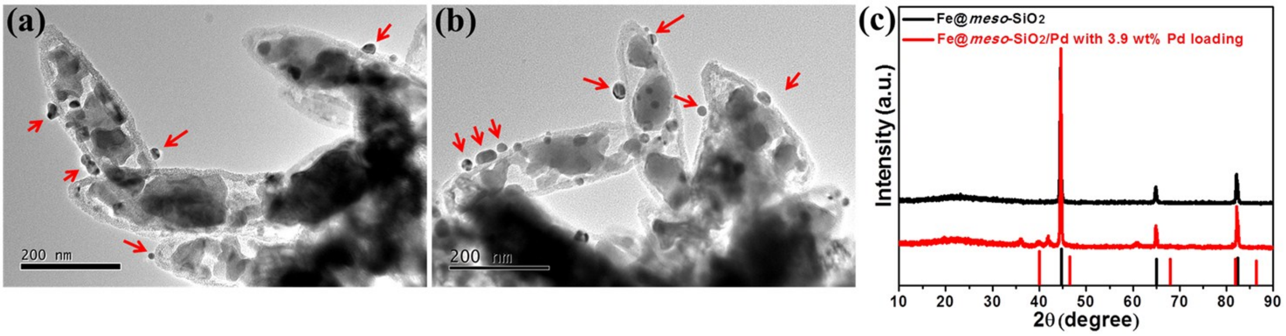


Fig. S6 TEM images (a-b) and XRD patterns (c) of the control sample Fe@*meso*-SiO$_2$/Pd with 3.9 wt% Pd loading. The red arrows in images (a) and (b) were used to locate the positions of Pd nanoparticles.

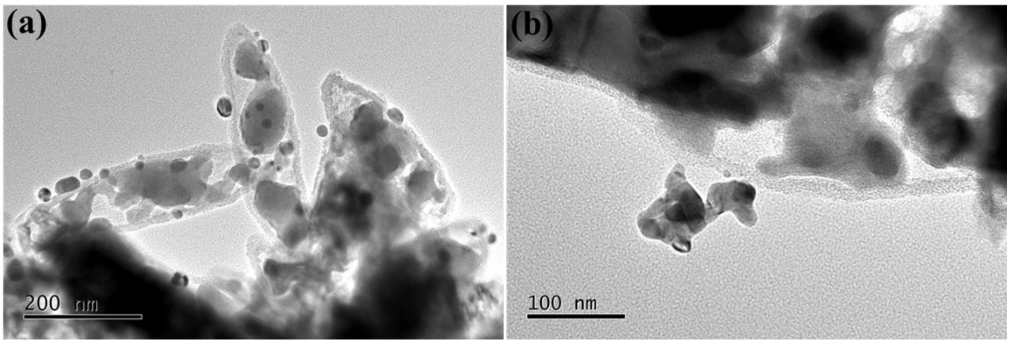


Fig. S7 TEM images of the control sample Fe@*meso*-SiO_2/Pd before (a) and after 20 runs (b).

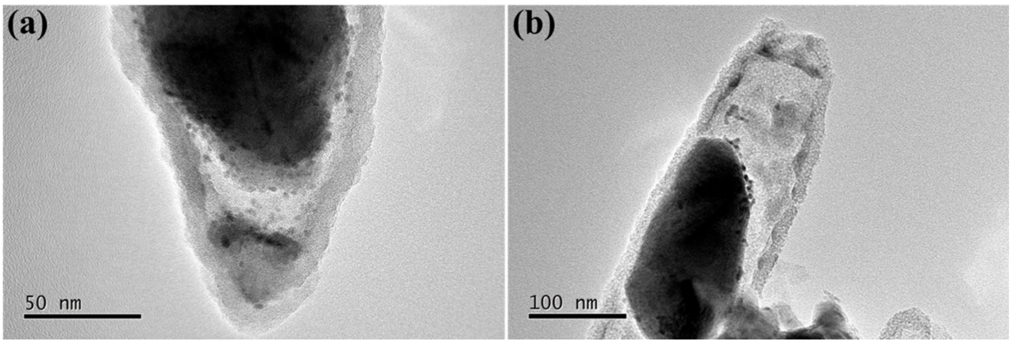


Fig. S8 TEM images of the fresh Pd-Fe@*meso*-SiO_2 (a) and recovered sample after 20th run (b) for styrene hydrogenation.

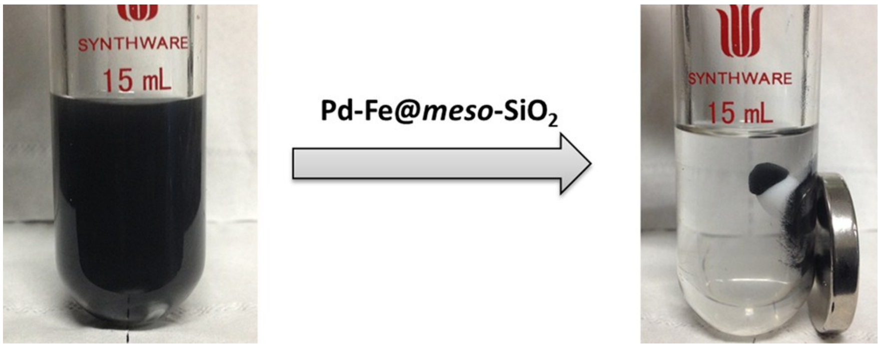


Fig. S9 Photograph of Pd-Fe@*meso*-SiO_2 with 2.7 wt % Pd loading dispersed in ethanol (left) and attracted by the magnet (right).

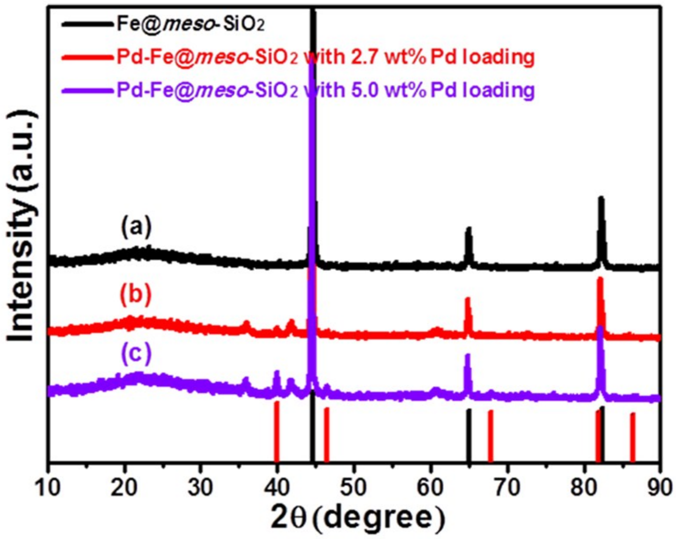


Fig. S10 XRD patterns of Fe@*meso*-SiO_2 (a), Pd-Fe@*meso*-SiO_2 with 2.7 wt% Pd loading (b) and Pd-Fe@*meso*-SiO_2 with 5.0 wt% Pd loading (c). Dark lines and red lines at the bottom were the standard Fe PDF card (JCPDS No. 06-0696) and Pd PDF card (JCPDS No. 88-2335), respectively.

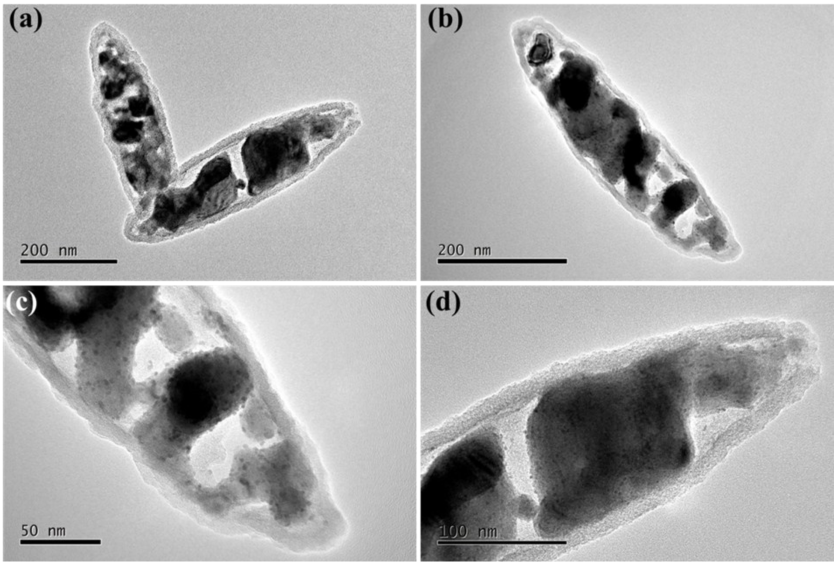


Fig. S11 TEM images of Pd-Fe@*meso*-SiO_2 with 5.0 wt% Pd loading.