

A Versatile Designed Synthesis of Magnetically Separable Nano-catalysts with Well-Defined Core-Shell Nanostructures

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Experimental Section

Chemicals

Anhydrous FeCl_3 , trisodium citrate, tetraethyl orthosilicate (TEOS), K_2PtCl_6 , PdCl_2 , ethanol, concentrated ammonia solution (28 wt %), ethylene glycol (EG), all the phenyl boronic acids, and the aryl halides were of analytical grade and purchased from Shanghai Chemical Corp. All chemicals were used as received. Deionized water was used for all experiments.

Synthesis of Fe_3O_4 particles

The water dispersible Fe_3O_4 particles were synthesized according to the method reported previously. Briefly, FeCl_3 (2.6 g, 16 mmol), trisodium citrate (1.0 g, 3.4 mmol) and sodium acetate (NaAc) (4.0 g, 48.8 mmol) were dissolved in ethylene glycol (80 mL) with magnetic stirring. The obtained yellow solution was then transferred and sealed into a Teflon-lined stainless-steel autoclave (200 mL in capacity). The autoclave was heated at 200 °C for 10 h, and then allowed to cool to room temperature. The black products were washed with ethanol and deionized water for 3 times, respectively.

Synthesis of $\text{Fe}_3\text{O}_4@C$ microspheres

The $\text{Fe}_3\text{O}_4@C$ microspheres were synthesized through a versatile hydrothermal method as follows. All the obtained Fe_3O_4 particles above was added to 60 mL 0.25 M Glucose solution, and then transferred and sealed into a Teflon-lined stainless-steel autoclave (100 mL in capacity). The autoclave was heated at 180 °C for 4 h, and then allowed to cool to room temperature. The obtained black products $\text{Fe}_3\text{O}_4@C$ were washed with deionized water for 3 times.

Deposition of Pd (or Pt) nanoparticles on $\text{Fe}_3\text{O}_4@C$ microspheres

In an optimized deposition process, 1 mL 0.01 M PdCl_2 ethanol dispersion was added to a 100 mL 1:1 water/ethanol mixed solution containing $\text{Fe}_3\text{O}_4@C$ microspheres (0.02 g/mL). Then the obtained mixture was subjected to 100 °C for 50 min, and then allowed to cool to room temperature. The obtained brown products $\text{Fe}_3\text{O}_4@C\text{-Pd}$ were washed with deionized water for 3 times. Similar procedure was carried out for the deposition of Pt nanoparticles just replacing the 1 mL 0.01 M PdCl_2

ethanol dispersion into 1 mL 0.01 M K_2PtCl_6 ethanol dispersion. Finally, black products $Fe_3O_4@C-Pt$ could be obtained.

Synthesis of $Fe_3O_4@C@Pd@mSiO_2$ Microspheres

To grow a mesoporous silica shell on the $Fe_3O_4@C-Pd$ (or $Fe_3O_4@C-Pt$) microspheres, the as-made $Fe_3O_4@C-Pd$ (or $Fe_3O_4@C-Pt$) microspheres (0.20 mg) were employed as seeds and redispersed in a mixed solution containing CTAB (0.45 g, 1.2 mmol), deionized water (100 mL), concentrated ammonia solution (2.0 mL, 28 wt %), and ethanol (150 mL). The resultant mixed solution was ultrasonicated for 5 min and then mechanically stirred for 30 min to form a uniform dispersion. Subsequently, 1.5 mL of TEOS was added dropwise to the dispersion under continuous stirring. After stirring for 6 h at 30 °C, the product was collected with a magnet and washed repeatedly with ethanol and deionized water. Finally, the purified microspheres were redispersed in 100 mL of acetone and refluxed at 80 °C for 48 h to remove the template CTAB. The extraction was repeated 4 times to ensure a complete removal of CTAB templates. Finally, the products were washed with deionized water, and $Fe_3O_4@C-Pd@mSiO_2$ (or $Fe_3O_4@C-Pt@mSiO_2$) microspheres with 35 nm-thick mesoporous silica were obtained.

Suzuki-Miyaura Cross-coupling Reactions

The $Fe_3O_4@C-Pd@mSiO_2$ catalyst (23 mg, 1.5 mol % of Pd), phenylboronic acid (1.50 mmol), base (1.00 mmol) and the aryl halide (1.00 mmol) were added to a reaction tube containing a magnetic stirrer bar in air; the solvent (1.5 mL) was then added. The reaction was stirred at the 70 °C for 6 hours. After cooling to room temperature, the mixture was extracted by DCM (2 x 5 mL) and filtered. The solvent of filtrate was removed in rotary evaporator and the crude product was directly used for chromatographic separation or dissolved by $CDCl_3$ for 1H -NMR analysis.

Measurements and characterizations

Transmission electron microscopy (TEM) images were taken with a JEOL 2011 microscope (Japan) operated at 200 kV. Samples were first dispersed in ethanol and then collected using carbon-film-covered copper grids for analysis. Scanning electronic microscopy (SEM) images were recorded on a Philips XL30 electron

microscope (Netherlands) operating at 20 kV. A thin gold film was sprayed on the sample before measurements. Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advanced X-ray diffractometer (Germany) with Ni-filtered Cu K α radiation (40 kV, 40 mA). Nitrogen sorption isotherms were measured at 77 K with a Micromeritics ASAP 2420 analyzer (USA). Before measurements, the sample were degassed in a vacuum at 200 °C for 10 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface area (S_{BET}) using adsorption data in a relative pressure range from 0.05 to 0.25. By using the Barrett-Joyner-Halenda (BJH) model, the pore volume and pore size distribution were derived from the adsorption branche of isotherms, and the total pore volume (V_{T}) was estimated from the adsorbed amount at a relative pressure P/P_0 of 0.992. The metal content in the Fe₃O₄@C@Pd@mSiO₂ sample were measured by using inductively coupled plasma-atomic emission spectrometry (ICP-AES, Varian VISTA-MPX).

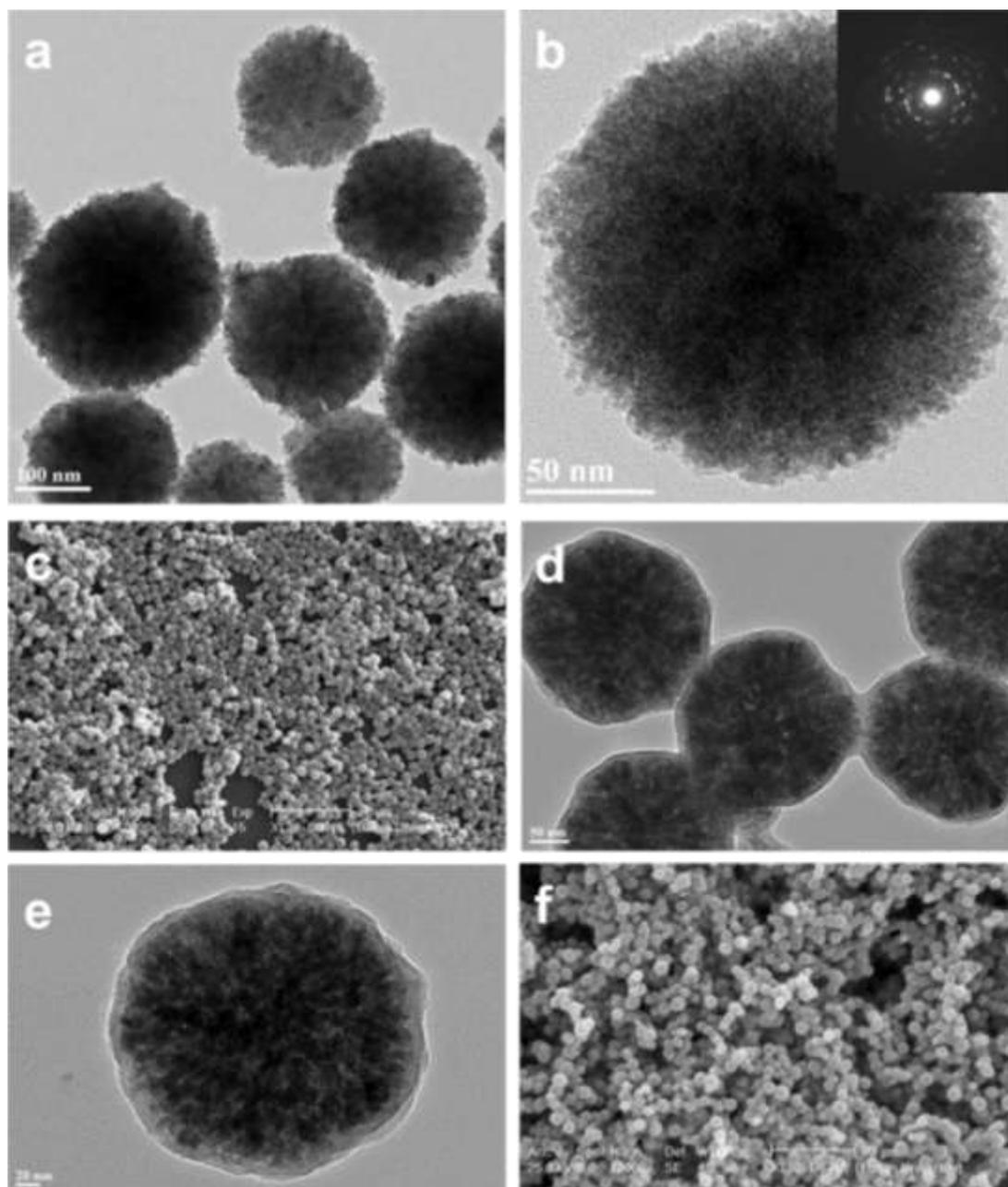


Figure S1. High-resolution TEM (HRTEM) images (a, b and d, e) and SEM image (c and f) of the magnetite particles before (a-c) and after (d-f) the carbon coating. There were numerous magnetite nanocrystals can be visible in images (a) and (b), indicating polycrystalline feature of the magnetite particles. In images (d) and (e), a thin layer of carbon shell can be clearly seen, suggesting the magnetic cores were well protected.

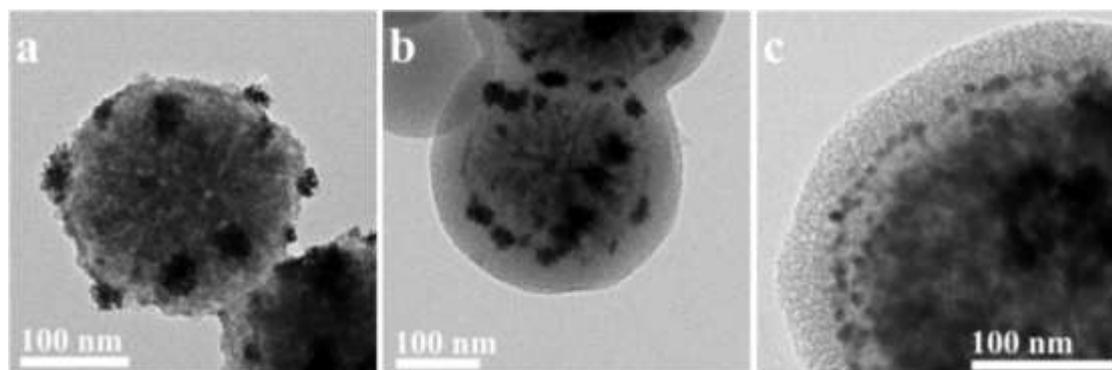


Figure S2. TEM images of Pt nanoparticles decorated $\text{Fe}_3\text{O}_4@C\text{-Pt}$ microspheres before (a) and after (b) mesoporous silica coating. Different from the sample $\text{Fe}_3\text{O}_4@C\text{-Pd}$, Pt nanoparticles were aggregated forming several Pt clusters on the surface of obtained microspheres. Image (c) shows the high resolution TEM image of sample $\text{Fe}_3\text{O}_4@C\text{-Pd@mSiO}_2$.

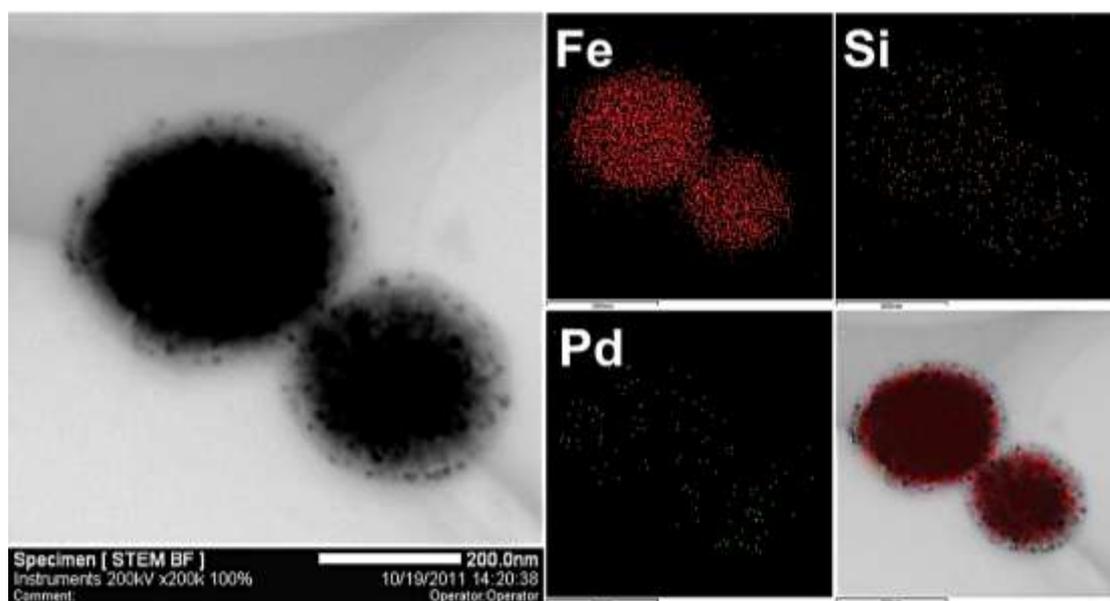


Figure S3. The EDX elemental mapping Images for $\text{Fe}_3\text{O}_4@C\text{-Pd@mSiO}_2$ microspheres on Fe, Si and Pd, providing the visual evidence on the distribution of these three elements.

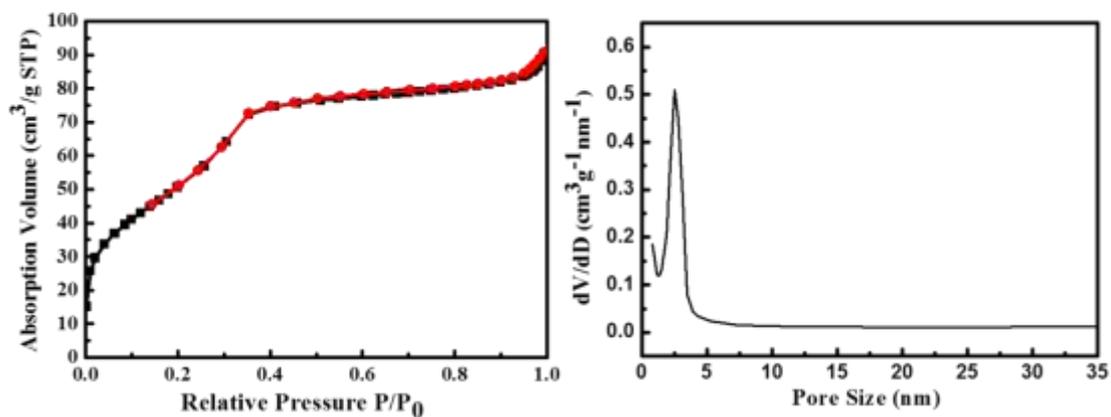


Figure S4. The nitrogen adsorption-desorption isotherms (left) and pore size distribution (right) of the Fe₃O₄@C-Pd@mSiO₂ microspheres with a 35-nm thick mesoporous silica layer after removing CTAB surfactant template by extraction of acetone.

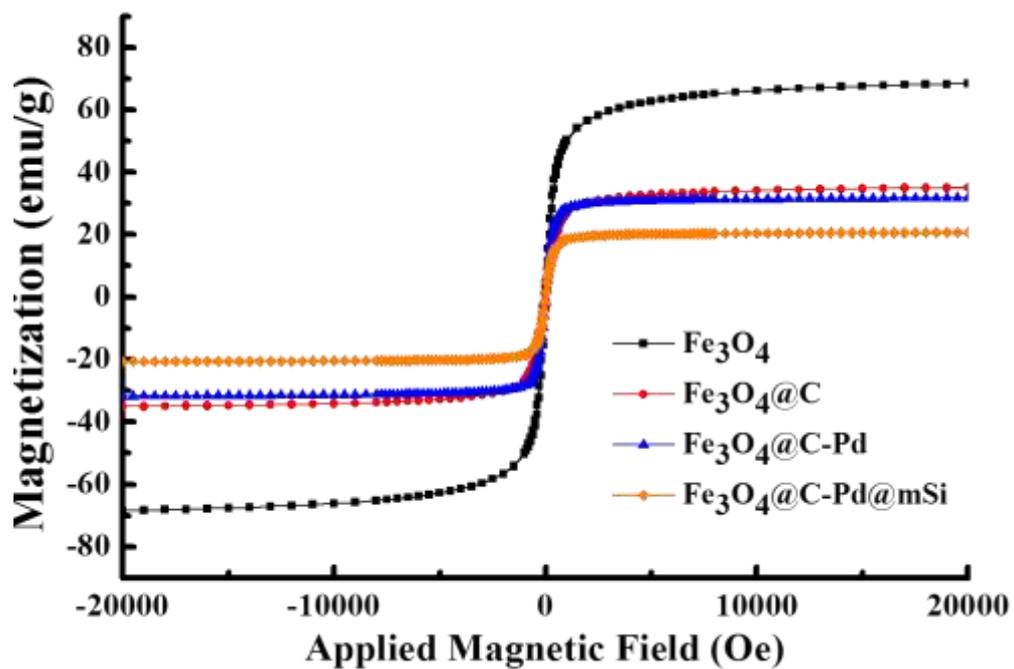


Figure S5. The magnetic hysteresis loops of the Fe₃O₄ particles (black), the core-shell Fe₃O₄@C microspheres (red), the Fe₃O₄@C-Pd microspheres (blue) and the Fe₃O₄@C-Pd@mSiO₂ microspheres (orange) with mesoporous silica layer.

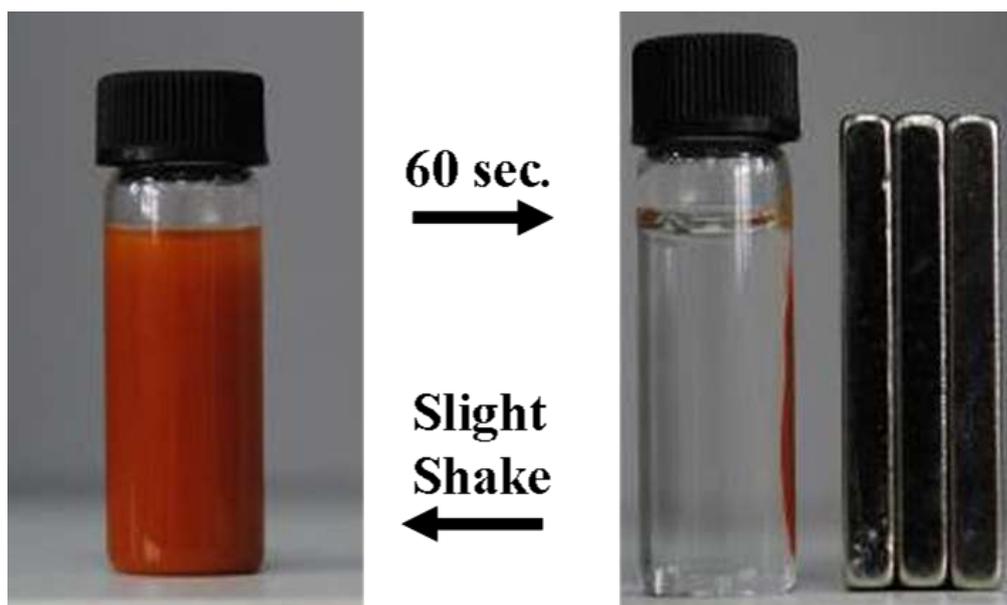


Figure S6. The magnetic separation process of $\text{Fe}_3\text{O}_4@\text{C-Pd@mSiO}_2$ microspheres achieved by a hand-held magnet.

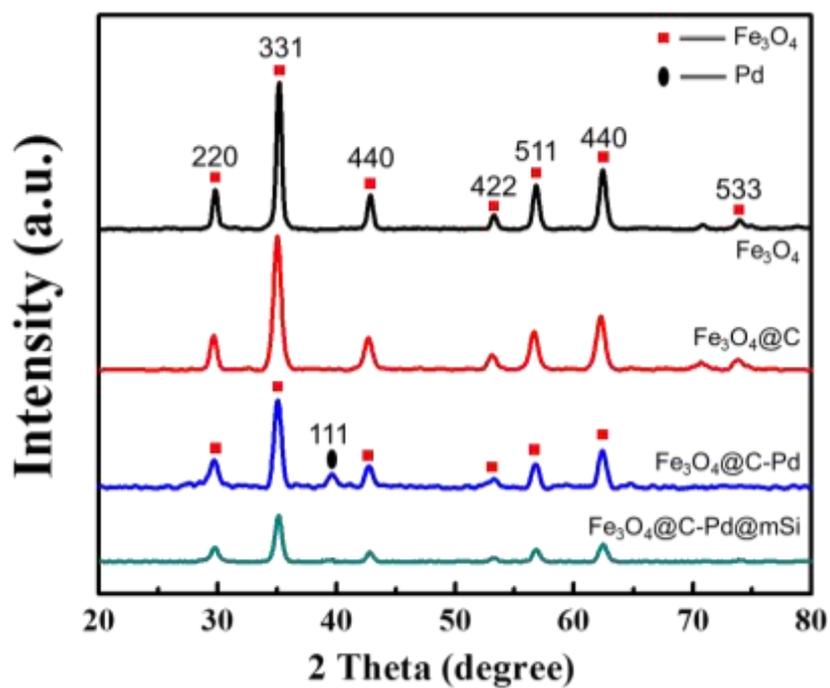


Figure S7. The wide-angle XRD patterns of (black) Fe_3O_4 particles, (red) $\text{Fe}_3\text{O}_4@C$ microspheres, (blue) $\text{Fe}_3\text{O}_4@C\text{-Pd}$ microspheres and (cyan) $\text{Fe}_3\text{O}_4@C\text{-Pd@mSi}_2$ microspheres.

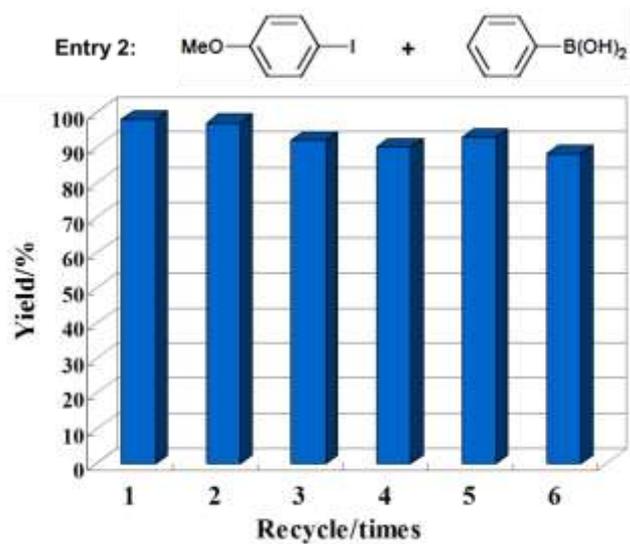


Figure S8. The chart of yield correlating with the number of reuse cycles, indicating the reusability of the $\text{Fe}_3\text{O}_4@\text{C-Pd@mSiO}_2$ as catalyst for the Suzuki-Miyaura cross-coupling reactions.