Supplementary Information

# Metallic nanoparticles immobilized in magnetic metal-organic frameworks: preparation and application as highly active, magnetically isolable and reusable catalysts

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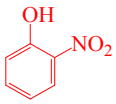
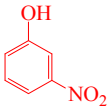
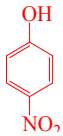
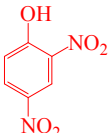
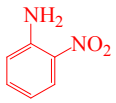
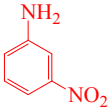
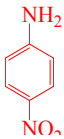
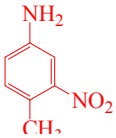
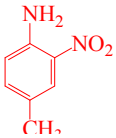
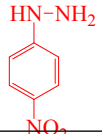
**Table S1.** Elemental and ICP analyses for the samples.

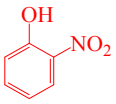
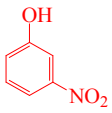
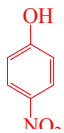
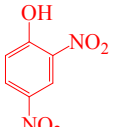
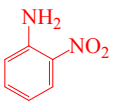
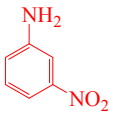
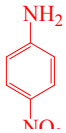
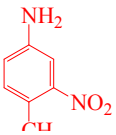
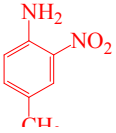
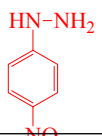
| Sample | Found (%) |
|---|---|
| $Fe_3O_4$@Pt/MIL-100 (Fe) (15 cycles) | C, 9.15; H, 1.27; Fe, 45.49; Pt, 4.26 |
| $Fe_3O_4$@Pt/MIL-100 (Fe) (20 cycles) | C, 10.06; H, 1.39; Fe, 43.99; Pt, 4.29 |
| $Fe_3O_4$@Pt/MIL-100 (Fe) (30 cycles) | C, 14.02; H, 1.76; Fe, 39.22; Pt, 4.07 |
| $Fe_3O_4$@Pt/MIL-100 (Fe) (40 cycles) | C, 15.61; H, 2.01; Fe, 36.38; Pt, 3.93 |
| $Fe_3O_4$@Pt/MIL-100 (Fe) (60 cycles) | C, 19.73; H, 2.41; Fe, 30.02; Pt, 3.67 |

**Table S2.** Reduction of various nitrobenzenes using $Fe_3O_4$@Au/MIL-100 (Fe) catalyst [a].

| Entry | Compound | Structure | Time/min | Conversion (%) | TOF ($h^{-1}$) |
|---|---|---|---|---|---|
| 1 | *o*-Nitrophenol |  | 15 | 93.2 | 144 |
| 2 | *m*-Nitrophenol |  | 6 | 96.8 | 374 |
| 3 | *p*-Nitrophenol |  | 10 | 96.2 | 223 |
| 4 | 2,4-Dinitrophenol |  | 44 | 96.2 | 51 |
| 5 | *o*-Nitroaniline |  | 10.5 | 95.2 | 210 |
| 6 | *m*-Nitroaniline |  | 9 | 96.5 | 249 |
| 7 | *p*-Nitroaniline |  | 20.5 | 96.6 | 109 |
| 8 | 4-Methyl-3-nitroaniline |  | 16.5 | 90.1 | 127 |
| 9 | 4-Methyl-2-nitroaniline |  | 39 | 96.2 | 57 |
| 10 | *p*-Nitrophenylhydrazine |  | 10.5 | 93.9 | 208 |

[a] Reaction condition: 25 μL of 10 mM nitrobenzene, 25 μL of 1.0 mg/mL catalyst, and 200 μL of 100 mM fresh $NaBH_4$.

**Table S3.** Reduction of various nitrobenzenes using $Fe_3O_4$@Pd/MIL-100 (Fe) catalyst [a].

| Entry | Compound | Structure | Time/min | Conversion | TOF ($h^{-1}$) |
|---|---|---|---|---|---|
| 1 | *o*-Nitrophenol |  | 2 | 94.6 | 778 |
| 2 | *m*-Nitrophenol |  | 1 | 94.2 | 1550 |
| 3 | *p*-Nitrophenol |  | 1.2 | 95.2 | 1343 |
| 4 | 2,4-Dinitrophenol |  | 13.5 | 97.3 | 119 |
| 5 | *o*-Nitroaniline |  | 2.5 | 97.3 | 641 |
| 6 | *m*-Nitroaniline |  | 2 | 93.4 | 768 |
| 7 | *p*-Nitroaniline |  | 4 | 97.6 | 401 |
| 8 | 4-Methyl-3-nitroaniline |  | 6 | 93.5 | 256 |
| 9 | 4-Methyl-2-nitroaniline |  | 9 | 92.6 | 169 |
| 10 | *p*-Nitrophenylhydrazine |  | 6 | 96.4 | 264 |

[a] Reaction condition: 25 μL of 10 mM nitrobenzene, 25 μL of 1.0 mg/mL catalyst, and 200 μL of 100 mM fresh $NaBH_4$.

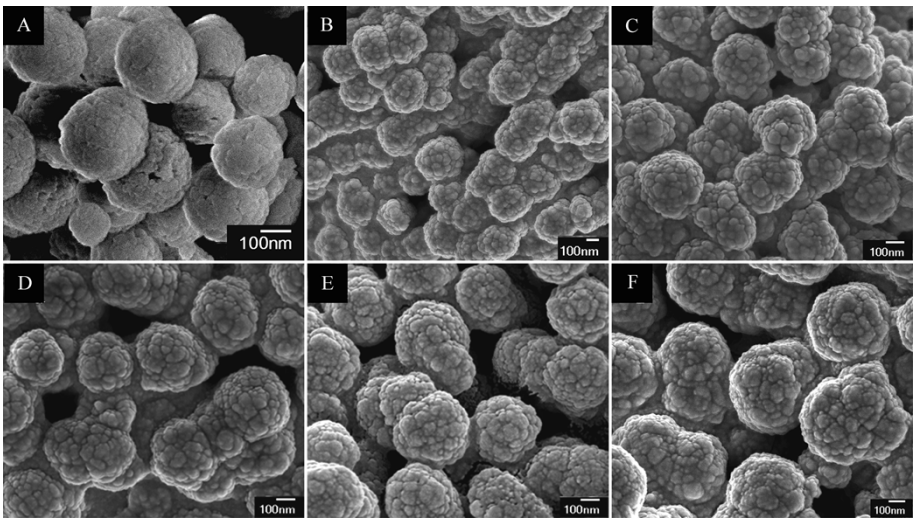



**Figure S1.** SEM images of (A) $Fe_3O_4$ and $Fe_3O_4$@MIL-100 (Fe) core-shell microspheres after (B) 15, (C) 20, (D) 30, (E) 40, and (F) 60 assembly cycles.

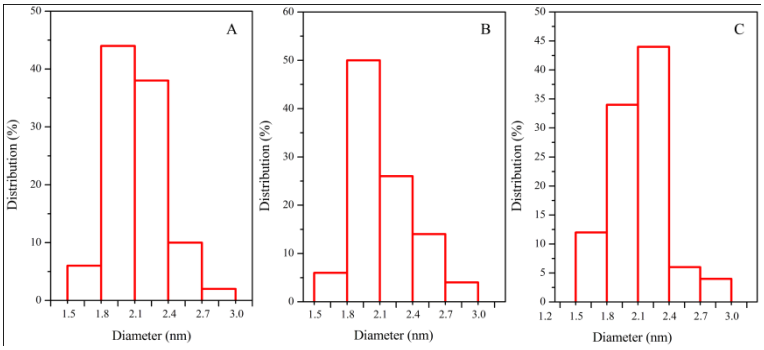



**Figure S2**. Size distribution of (A) Au NPs, (B) Pt NPs and (C) Pd NPs.

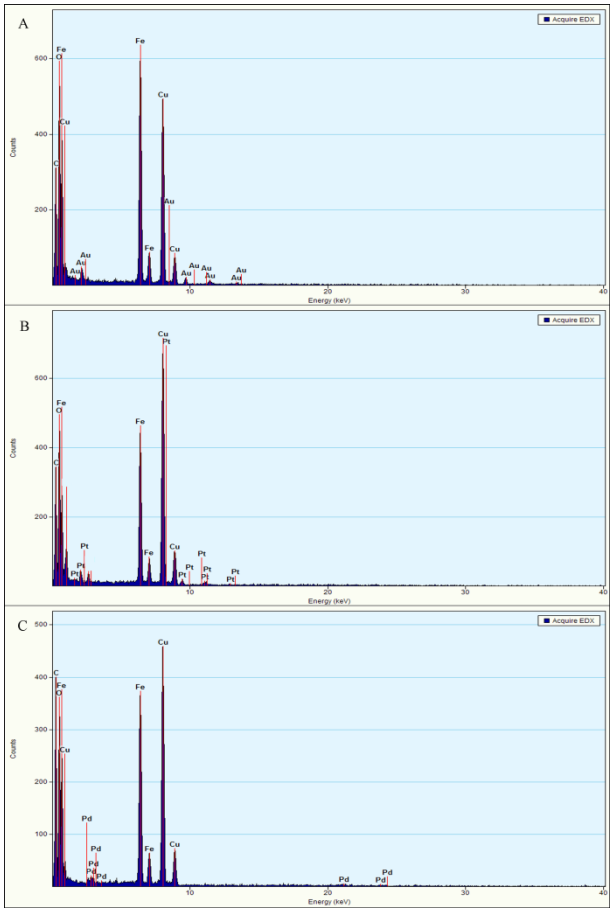



**Figure S3.** EDX spectra of the $Fe_3O_4$@MIL-100 (Fe) microspheres with 20 assembly cycles after embedded with (A) Au, (B) Pt, (C) Pd NPs. The copper signal originates from Cu grid.

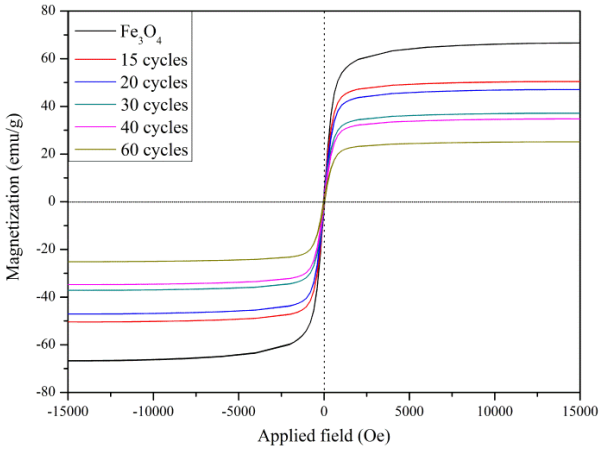



**Figure S4.** Room-temperature magnetic hysteresis loops of $Fe_3O_4$ and $Fe_3O_4$@MIL-100 (Fe) core-shell microspheres after 15, 20, 30, 40, and 60 assembly cycles.

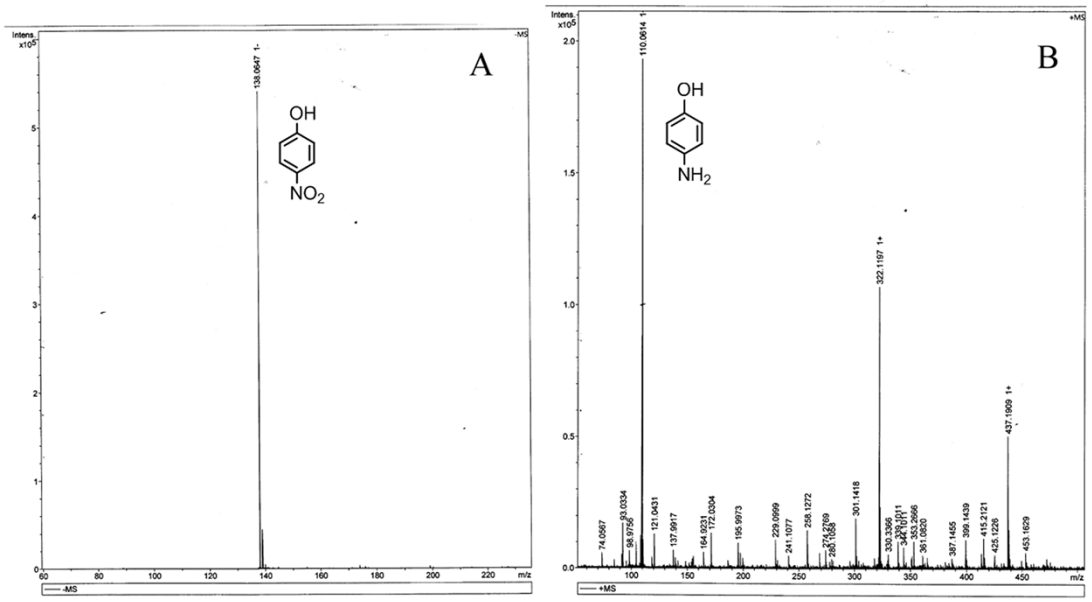



**Figure S5.** The gas chromatography-mass spectra of (A) *p*-nitrophenol and (B) the product of reduction reaction of *p*-nitrophenol.

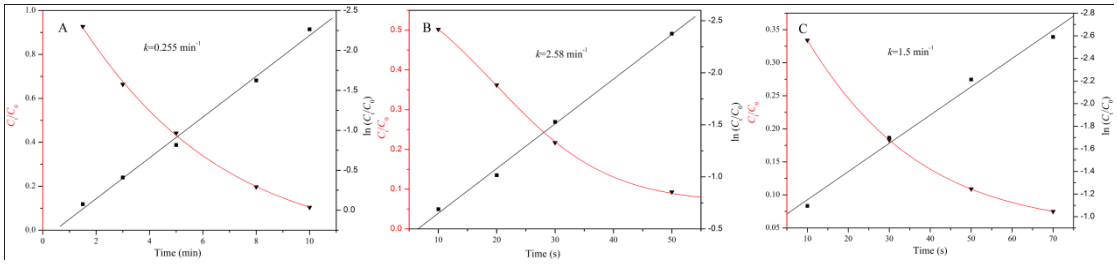



**Figure S6.** The $C_t/C_0$ (red) and ln ($C_t/C_0$) (black) *versus* the reaction time for the reduction of *p*-nitrophenol by $NaBH_4$ in presence of 25 μg catalyst: (A) $Fe_3O_4$@Au/MIL-100 (Fe), (B) $Fe_3O_4$@Pt/MIL-100 (Fe), and (C) $Fe_3O_4$@Pd/MIL-100 (Fe) with 20 assembly cycles. Conditions: *p*-nitrophenol] = 0.083 mM; [$NaBH_4$] = 6.67 mM, 25 °C.

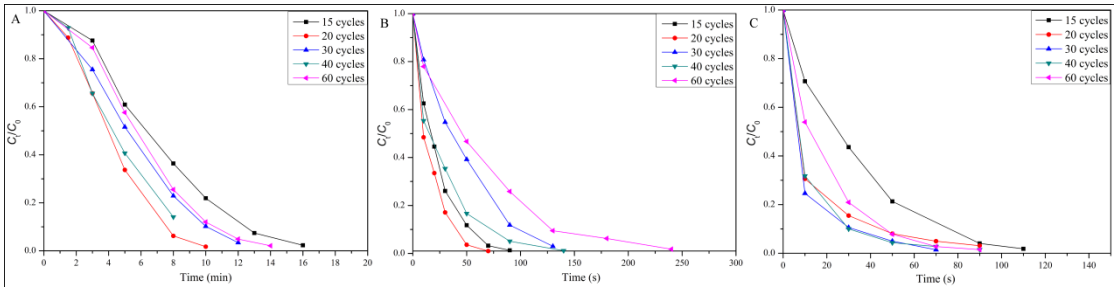



**Figure.** $C_t/C_0$ *versus* reaction time for the reduction of -nitrophenol with the catalysts: (A) $Fe_3O_4$@Au/MIL-100 (Fe), (B) $Fe_3O_4$@Pt/MIL-100 (Fe), and (C) $Fe_3O_4$@Pd/MIL-100 (Fe) after different assembly cycles.

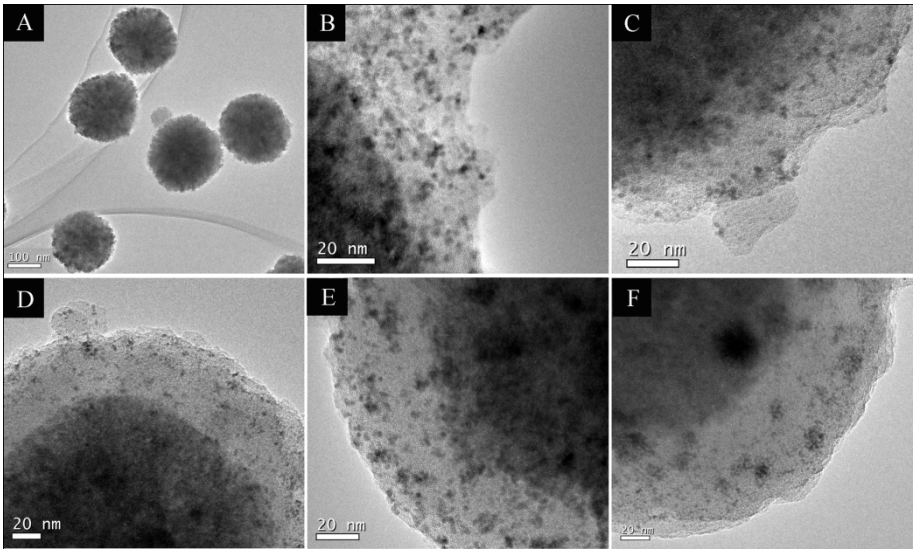



**Figure S8.** TEM images of individual (A) $Fe_3O_4$ and $Fe_3O_4$@Pt/MIL-100 (Fe) core-shell nanospheres after (B) 15, (C) 20, (D) 30, (E) 40, and (F) 60 assembly cycles.

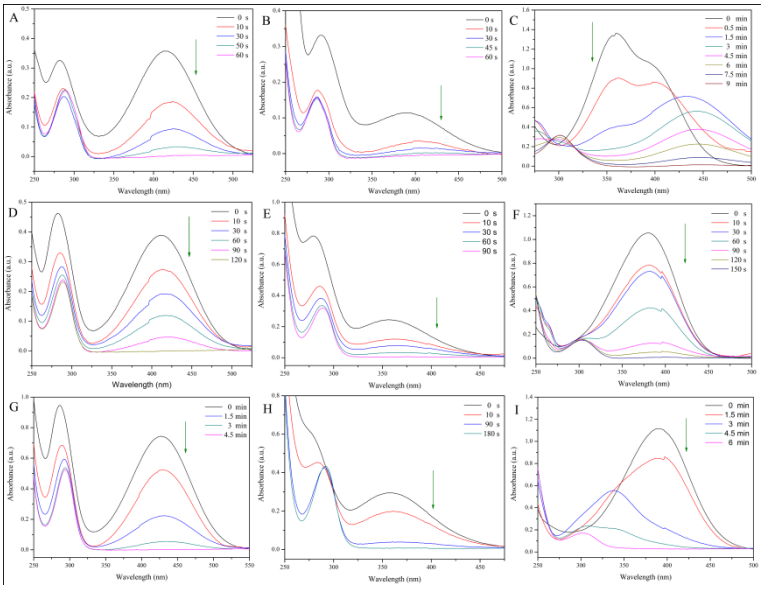


**Figure S9.** The UV-Vis absorption spectra change for the reduction process of (A) *o*-nitrophenol, (B) *m*-nitrophenol, (C) 2,4-dinitrophenol, (D) *o*-nitroaniline, (E) *m*-nitroaniline, (F) *p*-nitroaniline, (G) 4-Methyl-2-nitroaniline, (H) 4-Methyl-3-nitroaniline and (I) *p*-Nitrophenylhydrazine by $NaBH_4$ in the presence of $Fe_3O_4$@Pt/MIL-100 (Fe) catalyst.

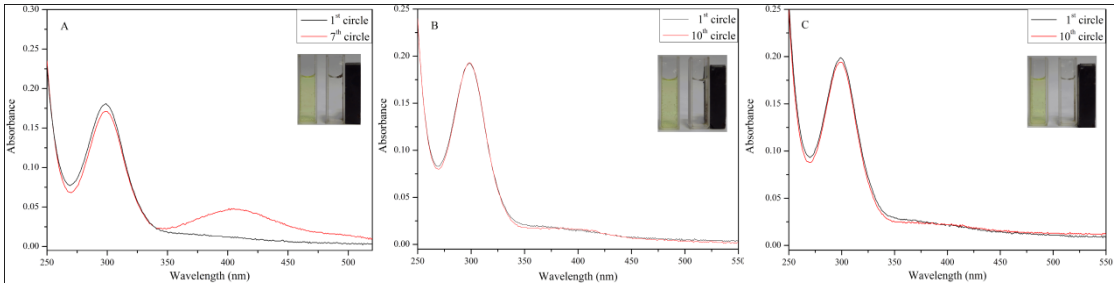



**Figure S10.** UV-Vis spectra of 4*p*-nitrophenol reduction with the as-prepared catalysts in different cycles: (A) $Fe_3O_4$@Au/MIL-100 (Fe), (B) $Fe_3O_4$@Pt/MIL-100 (Fe), and (C) $Fe_3O_4$@Pd/MIL-100 (Fe) with 20 assembly cycles. Inset showed the digital image of reaction solution after reaction for different cycles.

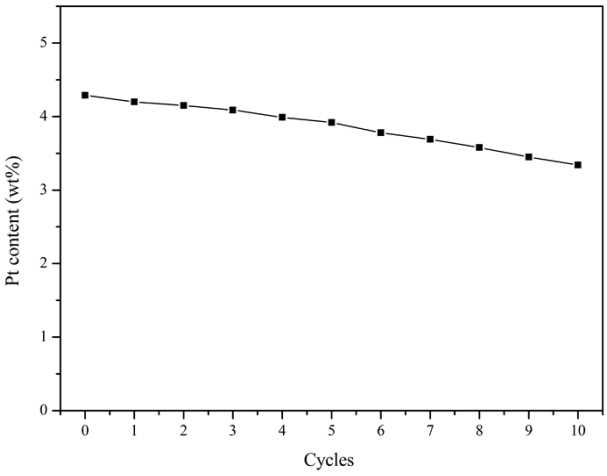



**Figure S11.** Changes of Pt content after each cycle.