

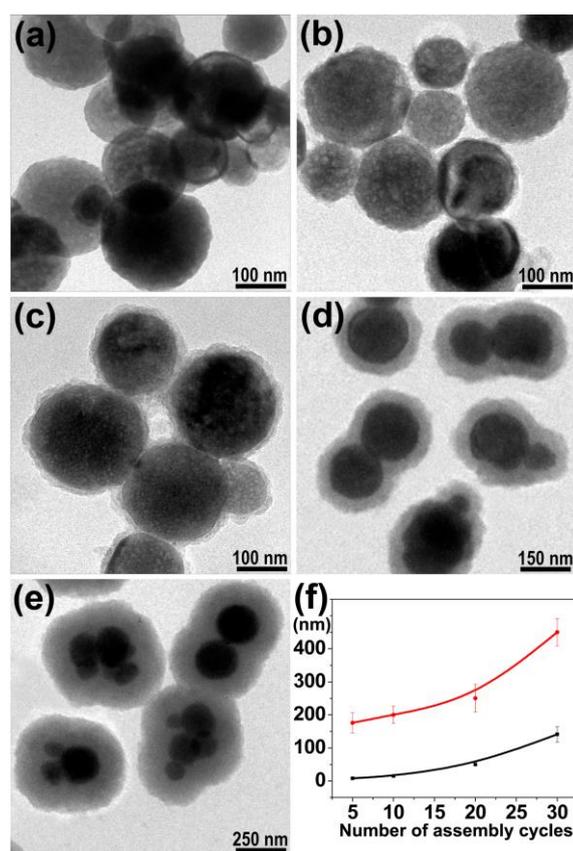
## Electronic Supplementary Information

# Multifunctional $\text{Au-Fe}_3\text{O}_4\text{@MOF}$ core-shell nanocomposite catalysts with controllable reactivity and magnetic recyclability

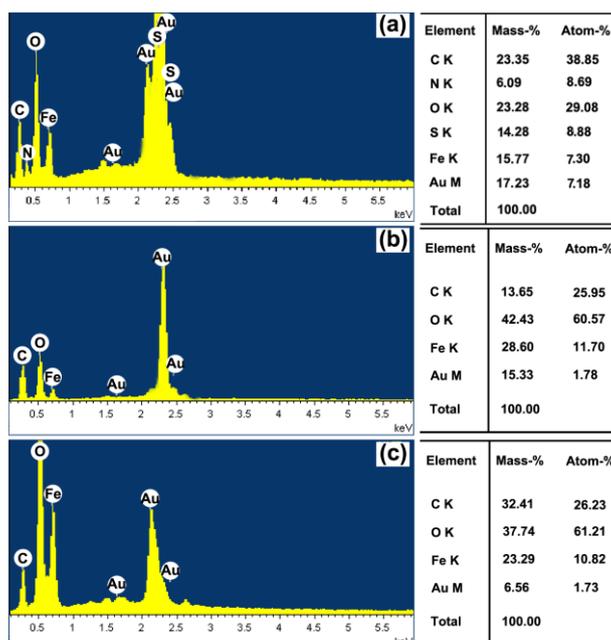
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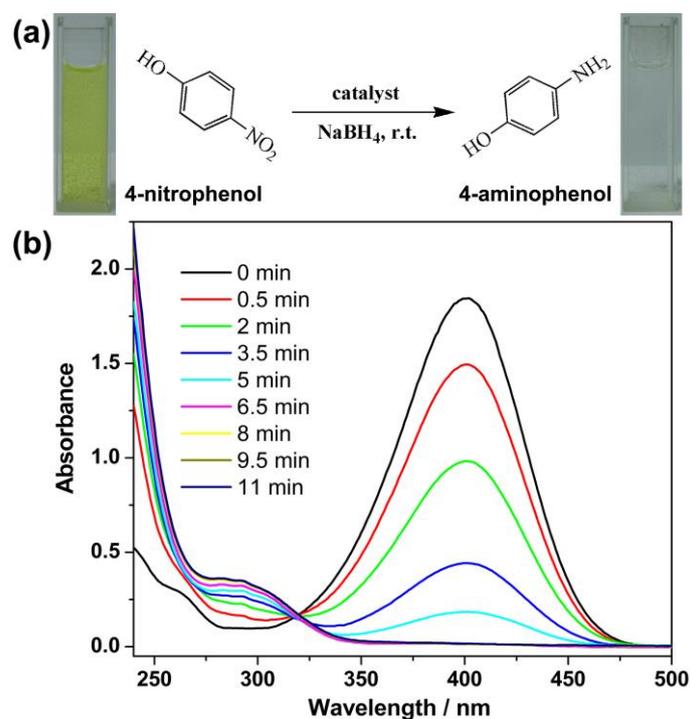
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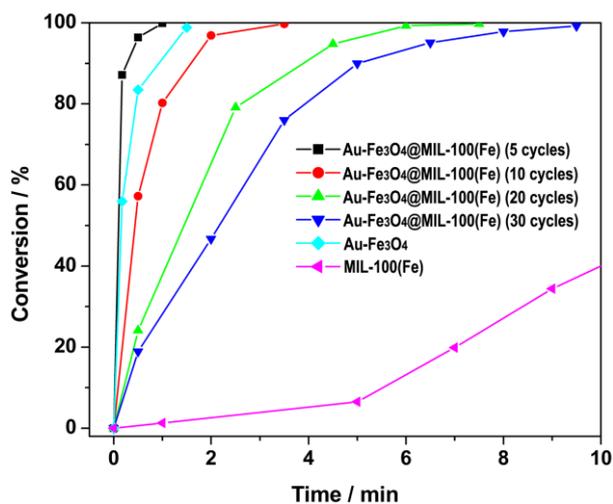
**Fig. S1** TEM images of  $\text{Au-Fe}_3\text{O}_4$  (a) and  $\text{Au-Fe}_3\text{O}_4\text{@MIL-100(Fe)}$  core-shell magnetic NPs after 5 (b), 10 (c), 20 (d), 30 (e) assembly cycles. (f) The correlations between the assembly cycles and the resulting diameter (red line) and shell thickness (black line).



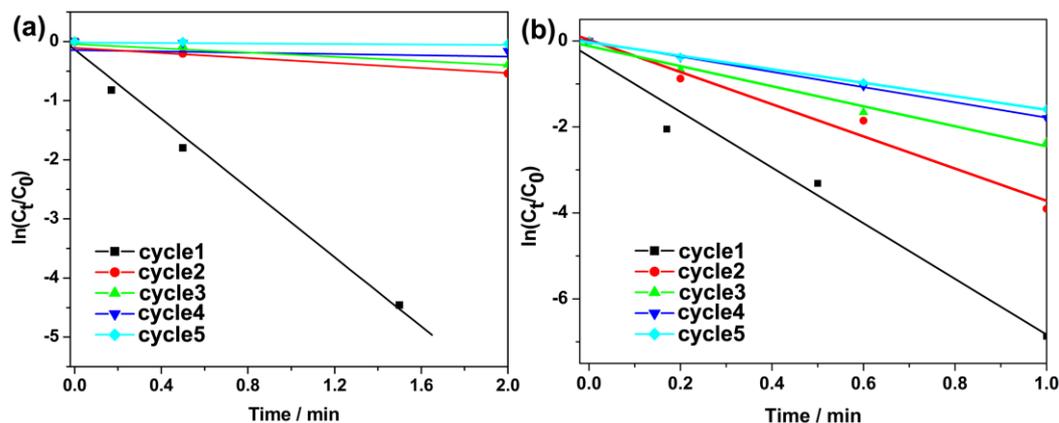
**Fig. S2** EDX spectra of Au-Fe<sub>3</sub>O<sub>4</sub> (a), Au-Fe<sub>3</sub>O<sub>4</sub>@MIL-100(Fe) core-shell magnetic NPs after 5 (b) and 30 assembly cycles (c).



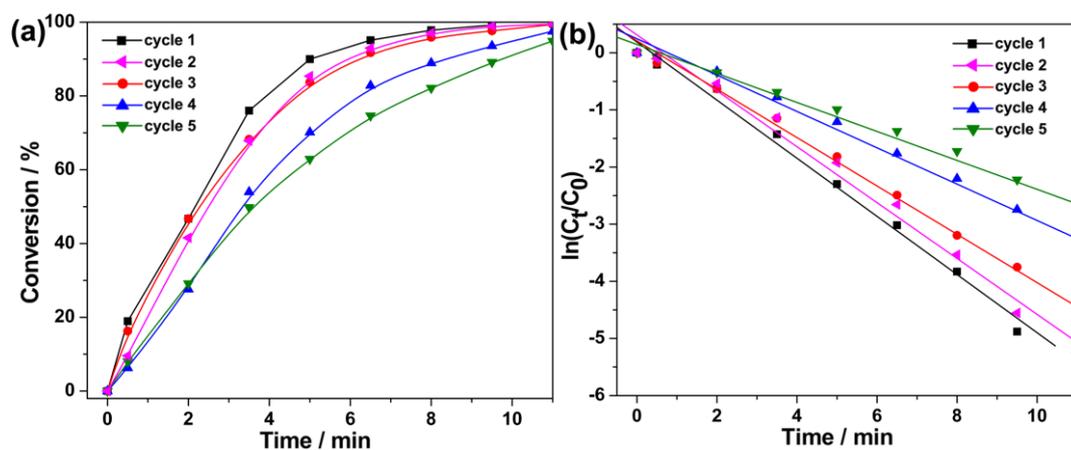
**Fig. S3** (a) The reaction scheme, associated photographs of the color change for conversion of 4-NP from bright yellow to colorless, and (b) UV-vis spectra of 4-NP reduction with Au-Fe<sub>3</sub>O<sub>4</sub>@MIL-100(Fe) core-shell NPs after 30 assembly cycles.



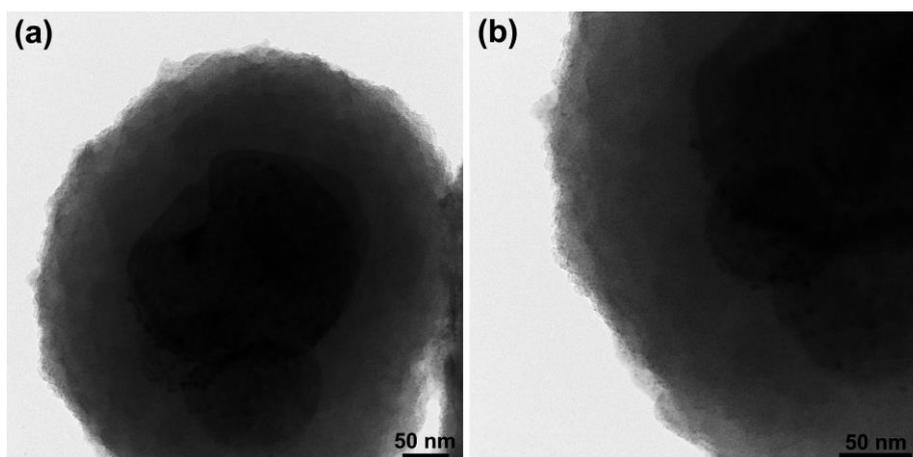
**Fig. S4** Catalytic conversion of 4-NP to 4-AP over Au-Fe<sub>3</sub>O<sub>4</sub>, MIL-100(Fe), and Au-Fe<sub>3</sub>O<sub>4</sub>@MIL-100(Fe) core-shell magnetic NPs after 5, 10, 20 and 30 assembly cycles, respectively.



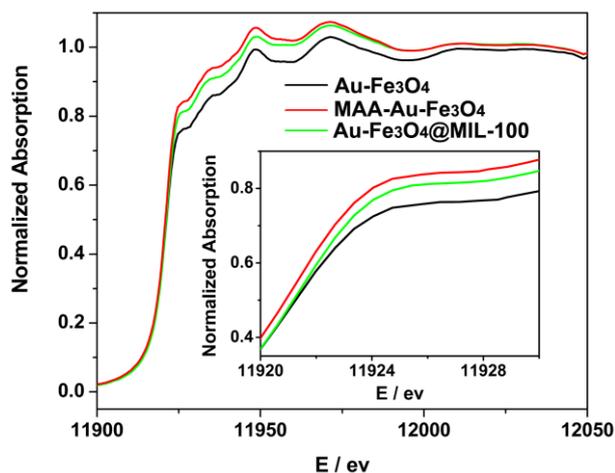
**Fig. S5** Relationship of the  $\ln(C_t/C_0)$  and reaction time  $t$  for 5 cycles of 4-NP reduction under the same reaction conditions over the Au-Fe<sub>3</sub>O<sub>4</sub> magnetic NPs (a), and the core-shell Au-Fe<sub>3</sub>O<sub>4</sub>@MIL-100(Fe) magnetic NPs synthesized with five assembly cycles (b).



**Fig. S6** Catalytic conversion (a) and relationship of the  $\ln(C_t/C_0)$  and reaction time  $t$  (b) for 5 cycles of 4-NP reduction over the core-shell Au-Fe<sub>3</sub>O<sub>4</sub>@MIL-100(Fe) magnetic NPs. The catalysts were synthesized with 30 assembly cycles.



**Fig. S7** TEM images (a,b) of the Au-Fe<sub>3</sub>O<sub>4</sub>@MIL-100(Fe) core-shell magnetic catalysts after the catalytic reaction. The catalysts were synthesized with 30 assembly cycles.



**Fig. S8** Au L<sub>3</sub>-edge XANES spectra for Au-Fe<sub>3</sub>O<sub>4</sub>, MMA-Au-Fe<sub>3</sub>O<sub>4</sub>, and Au-Fe<sub>3</sub>O<sub>4</sub>@MIL-100(Fe)

core-shell magnetic NPs. The insert shows the zoom-in lines.

**Table S1** Recovery and reuse of Au-Fe<sub>3</sub>O<sub>4</sub>.

Use	Yield (%)	<i>k</i> (min <sup>-1</sup> )
first	100	2.92
second	42	0.12
third	33	0.090
fourth	15	0.054
fifth	4	0.020

**Table S2** Recovery and reuse of Au-Fe<sub>3</sub>O<sub>4</sub>@MIL-100(Fe) core-shell magnetic nanocatalysts. The catalysts were synthesized with 5 assembly cycles.

Use	Yield (%)	<i>k</i> (min <sup>-1</sup> )
first	100	5.53
second	98	3.74
third	91	2.33
fourth	84	1.77
fifth	80	1.57

**Table S3** Recovery and reuse of Au-Fe<sub>3</sub>O<sub>4</sub>@MIL-100(Fe) core-shell magnetic nanocatalysts. The catalysts were synthesized with 30 assembly cycles.

Use	Yield (%)	<i>k</i> (min <sup>-1</sup> )
first	100	0.51
second	100	0.49
third	99	0.42
fourth	98	0.32
fifth	95	0.26

**Table S4** Fitting parameters of the Au L<sub>3</sub>-edge EXAFS oscillations for Au-Fe<sub>3</sub>O<sub>4</sub>, MAA-Au-Fe<sub>3</sub>O<sub>4</sub>, and Au-Fe<sub>3</sub>O<sub>4</sub>@MIL-100(Fe) core-shell magnetic NPs.

sample	bond	$R / \text{\AA}$	$N$	$\sigma^2 / \text{\AA}^2(10^{-3})$	$\Delta E$
Au-Fe <sub>3</sub> O <sub>4</sub>	Au-Au	$2.88 \pm 0.02$	$10.4 \pm 0.4$	$11.2 \pm 1.1$	$3.1 \pm 1.0$
	Au-S	$2.29 \pm 0.03$	$0.8 \pm 0.2$	$6.5 \pm 1.0$	$4.0 \pm 0.5$
MAA-Au-Fe <sub>3</sub> O <sub>4</sub>	Au-Au	$2.87 \pm 0.02$	$9.8 \pm 0.4$	$13.0 \pm 1.1$	$4.5 \pm 1.2$
	Au-S	$2.33 \pm 0.03$	$1.1 \pm 0.2$	$6.1 \pm 1.0$	$3.0 \pm 0.4$
Au-Fe <sub>3</sub> O <sub>4</sub> @MIL-100(Fe)	Au-Au	$2.87 \pm 0.02$	$10.1 \pm 0.4$	$12.7 \pm 1.1$	$2.9 \pm 1.1$
	Au-S	$2.33 \pm 0.03$	$1.0 \pm 0.2$	$6.2 \pm 1.0$	$3.5 \pm 0.5$