Electronic Supplementary Material (ESI) for Nanoscale.

Urchin-like hybrid nanostructures of CuOx/Fe2O3 from Cu-mediated pyrolysis of Fe-MOFs for catalytic reduction of organic pollutants

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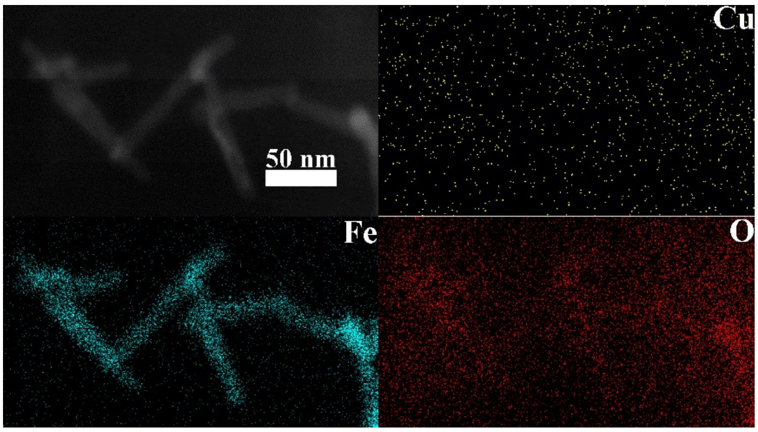

Figure S1 STEM, and EDS mapping of nanorods from Urchin-like CuO_x/Fe_2O_3.

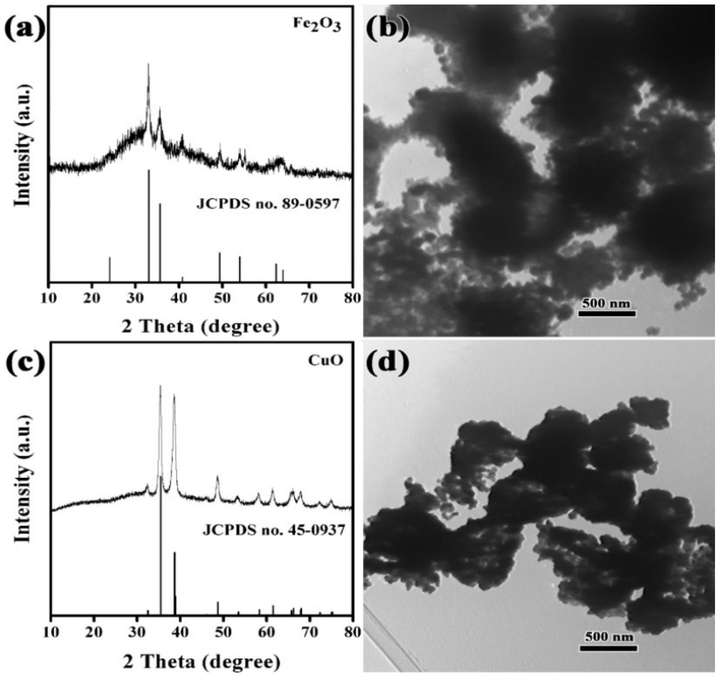

Figure S2 XRD patterns and TEM images: (a, b) Fe_2O_3 framework; (c, d) CuO nanocages.

(Synthesis of Fe_2O_3 and CuO: MIL-101 (Fe), HKUST-1 was directly annealed at 350 ^oC in air for 2 h with a heating rate of 1 ^oC min^{-1}, respectively.)

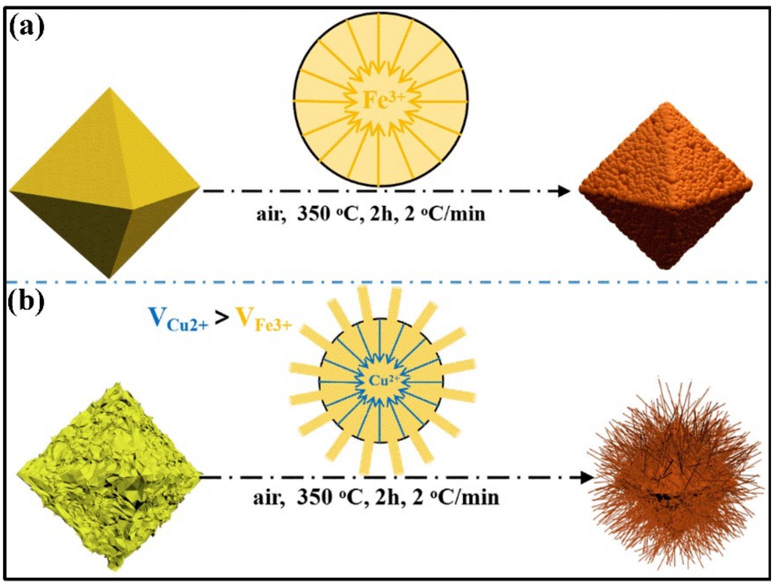

Figure S3 Diagram of formation mechanism: (a) MIL-101-Fe derived Fe_2O_3; (b) $Cu(NO_3)_2$/MIL-101-Fe derived CuO_x/Fe_2O_3.

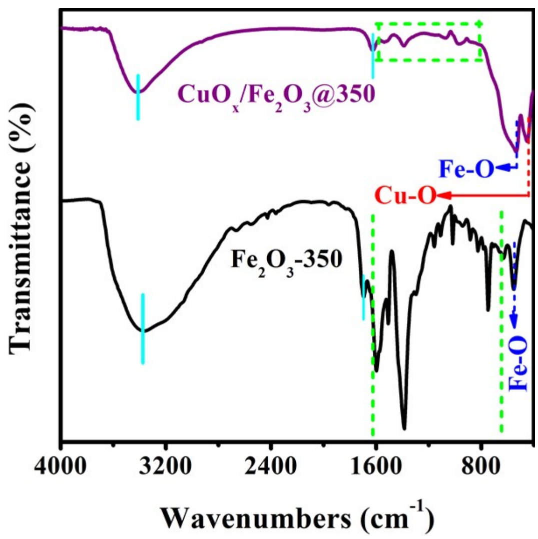

Figure S4 FT-IR spectra of CuO_x/Fe_2O_3@350 and Fe_2O_3@350.

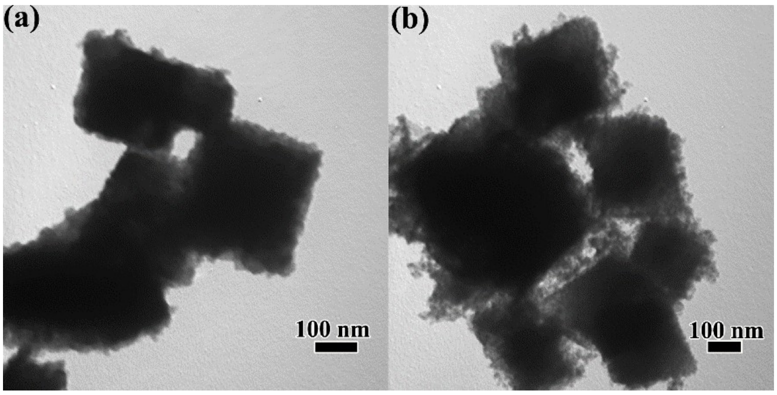

Figure S5 TEM images: (a) $Ni(NO_3)_2$/MIL-101-Fe derived Ni-Fe Oxide; (b) $Co(NO_3)_2$/MIL-101-Fe derived Co-Fe Oxide.

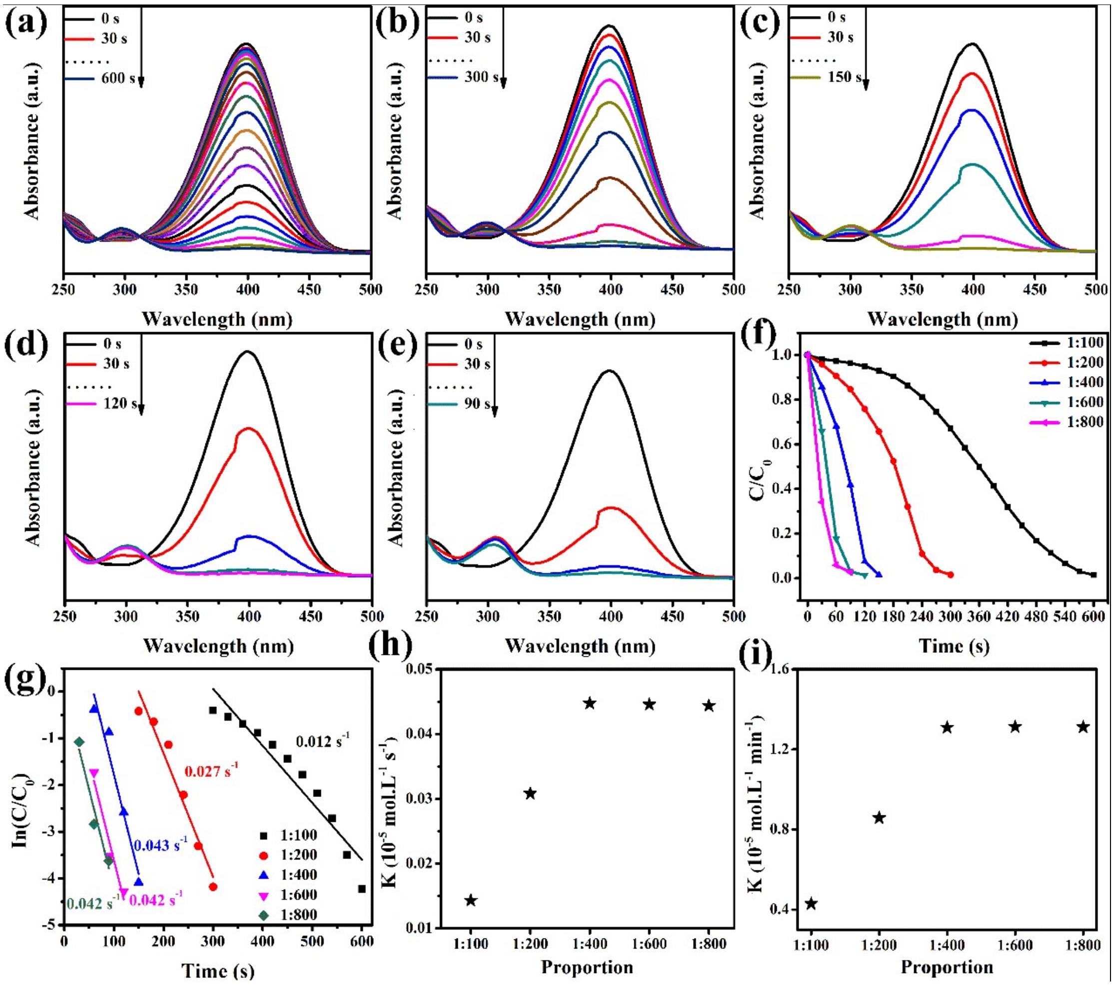

Figure S6 The reduction of 4-NP by CuO_x/Fe_2O_3@350 with different dose of $NaBH_4$: (a-e) UV-vis spectra; (f) Plots of C/C_0 *vs* t; (g) plots of ln(C/C_0) *vs* t; (h, i) Plots of constant rate vs proportion of 4-NP to $NaBH_4$.

Reduction conditions: 4-NP (3.0 mL, 0.12 mmol L^{-1}), catalyst (30 µL, 0.5 mg mL^{-1}), and temperature (298.15 K).

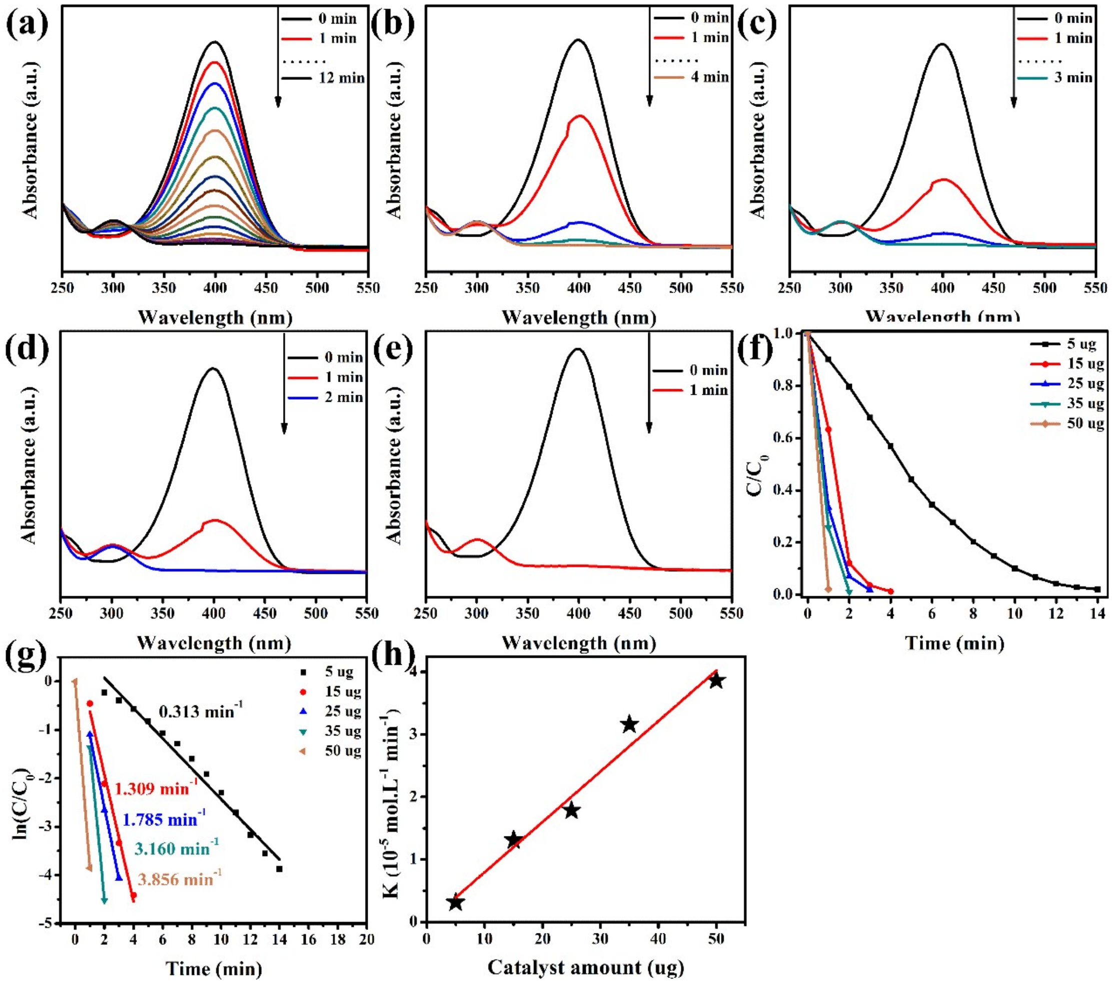

Figure S7 The reduction of 4-NP to 4-AP over different dose of CuO_x/Fe_2O_3@350: (a-e) UV-vis spectra; (f) Plots of C/C_0 *vs* t; (g) Plots of ln(C/C_0) *vs* t; (h) Plots of constant rate *vs* catalyst dosage.

Reduction conditions: 4-NP (3.0 mL, 0.12 mmol L^{-1}), catalyst (0.5 mg mL^{-1}), $NaBH_4$ (0.12 mmol), and temperature (298.15 K).

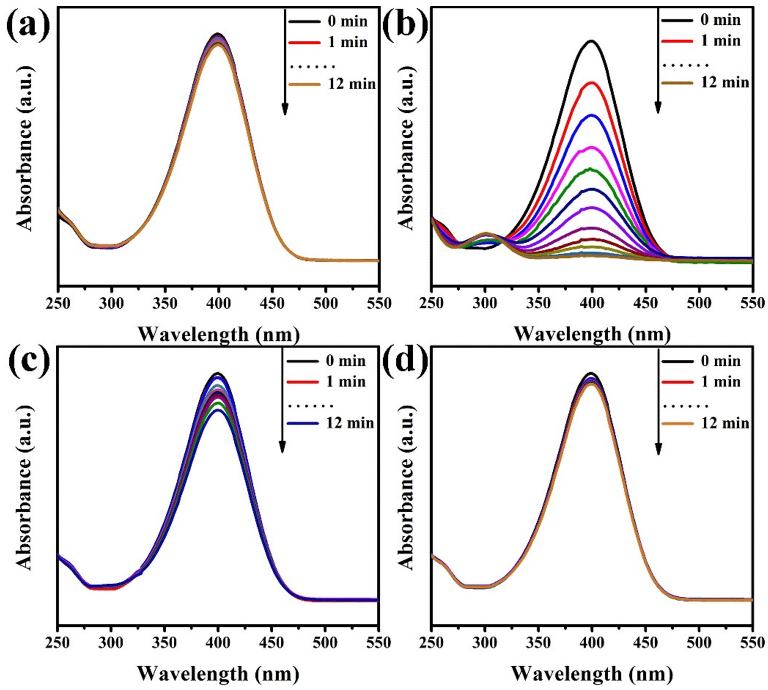

Figure S8 UV-vis spectra of reduction of 4-NP over CuO_x/Fe_2O_3 derived from $Cu(NO_3)_2$/MIL-101-Fe at different temperature: (a) 300 °C; (b) 350 °C; (c) 400 °C; (d) 450 °C.

Reduction conditions: 4-NP (3.0 mL, 0.12 mmol L^{-1}), catalyst (10 μL, 0.5 mg mL^{-1}), $NaBH_4$ (0.12 mmol), and temperature (298.15 K).

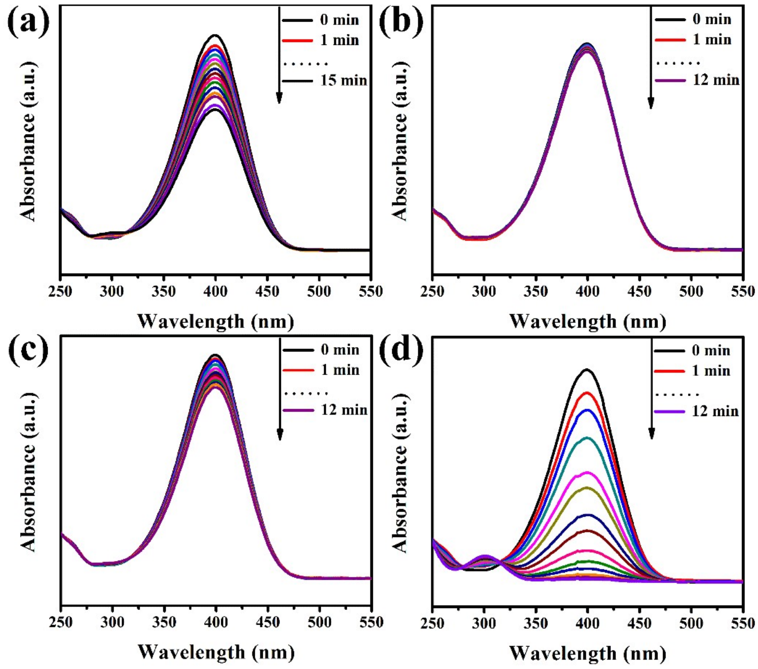

Figure S9 UV-vis spectra of reduction of 4-NP over different component catalyst: (a) CuO nanocage; (b) Fe_2O_3; (c) mixture of $CuO+Fe_2O_3$; (d) CuO_x/Fe_2O_3@350.

Reduction conditions: 4-NP (3.0 mL, 0.12 mmol L^{-1}), catalyst (10 μL, 0.5 mg mL^{-1}), $NaBH_4$ (0.12 mmol), and temperature (298.15 K).

Figure S10 Photograph of dye molecules before and after addition of $NaBH_4$ without catalysts.

Table S1 Comparison of catalytic results for the reduction of 4-NP by $NaBH_4$ in the presence of various catalysts.

Catalysts	4-NP (mM)	$NaBH_4$ (M)×10^{-2}	*Kinetic rate constant* K_{app} (min^{-1})	*Ratio constant* K (min^{-1} g^{-1})	*Turnover frequency* TOF (h^{-1})	*Reference*
CuO_x/Fe_2O_3@350	0.12	4.8	0.3122	6.244×10^4	574.5	**this work**
Ag-OMS-C	0.1	0.01	1.8	9.000×10^3	90.2	[S1]
Pd/C	1.67	120	0.52980	6.915×10^2	82.8	[S2]
Pt nanotubes	0.09	10	0.2	13.3		[S3]
PdPt nanotubes	0.09	10	0.5	33		[S3]
Au	0.103	1	0.126	21	0.00046	[S4]

The TOF is calculated by moles of reduced 4-NP molecules per mole copper of catalyst per hour.

Reference

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S2 Y. Fang and E. Wang, *Nanoscale* 2013, **5**, 1843-1848.

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