

Supporting Information for

Synthesis of ultrafine Co/CoO nanoparticles embedded in N-doped carbon framework magnetic material and application for 4-nitrophenol catalytic reduction

Dongsheng Wang,^{ab} Liang Xu,^a Fanming Zeng,^{*ab} Xiaoli Hu,^{ab} Bailing Liu,^{*ab} Chun Li,^a Zhongmin Su^{*abc} and Jing Sun^{ab}

^aSchool of Materials Science and Engineering, Changchun University of Science and Technology, Changchun 130022, China. Email: zengfm@cust.edu.cn

^bJilin Provincial Science and Technology Innovation Center of Optical Materials and Chemistry, Changchun. 130022, China. Email: liubl@cust.edu.cn

^cJoint Sino-Russian Laboratory of Optical Materials and Chemistry, Changchun 130022, China. Email: zmsu@nenu.edu.cn

Contents

1. Materials and measurements

2. Synthesis and methods

3. Characterizations and results

Table S1 Crystallographic data of **Co-MOF**.

Fig. S1 (a) The coordination environment of Co (II); (b) 3D structure diagram of **Co-MOF**; (c) The connection between the 2D planes of **Co-MOF**; (d) Topological diagram of **Co-MOF**.

Fig. S2 FTIR spectra (a), TGA curves pattern (b) and experimental and simulation XRD of **Co-MOF**.

Fig. S3 XPS analysis of **Co/CoO@NC**: (a) full spectra; High-resolution spectrum of (b) C 1s, (c) Co 2p and (d) N 1s.

Fig. S4 (a) Absorption peak of 4-NP (black) and after adding NaBH₄ (red); (b) Absorption peak of 4-AP after adding catalyst. UV-vis spectrum with only (c) 0.1 mg and (d) 1 mg catalyst added.

Table S2 Comparison of 4-NP reduction rate between **Co/CoO@NC** and some precious metal catalysts.

Fig. S5 Magnetic hysteresis loop of **Co/CoO@NC** (298 K).

Fig. S6 (a) XRD curve, (b) TEM picture and (c) EDX elemental mapping of **Co/CoO@NC** after five cycles experiment.

1. Materials and measurements

All chemicals are from commercial sources and used directly without purification. 4-nitrophenol (4-NP), sodium borohydride (NaBH_4), 2,4,6-Tri(4-pyridyl)-1,3,5-triazine (TPT), 1,4-naphthalenedicarboxylate (1,4-ndc) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were purchased from Energy Chemical. N,N-Dimethylacetamide (DMA) was obtained from Tokyo Chemical Industry.

The X-ray single crystal diffraction data was collected on a Bruker SMART APEX II single crystal instrument using a Mo target ($K\alpha$, $\lambda = 0.71073 \text{ \AA}$) at room temperature. Thermogravimetric analysis (TGA) was performed on the TA STD-Q600 thermal analyzer. The morphology of Co/CoO@NC was observed using a JEM-2100F field emission projection microscope with an accelerating voltage of 200 kV, and the phase composition was studied by X-ray diffraction (XRD) using Bruker D8 diffractometer. The specific surface area of Co/CoO@NC was calculated by the Brunauer-Emmett-Teller (BET) method, and the pore size distribution was evaluated using the Barrett-Joyner-Halenda (BJH) model. The elemental composition of Co/CoO@NC was analyzed by X-ray photoelectron spectroscopy (XPS) of KRATOS Analytical. Monitor the progress of the catalytic reduction reaction on the JASCO V-770 UV-Vis spectrometer.

2. Synthesis and Methods

Synthesis of Co-MOF. The mixture of TPT (10.4 mg, 0.03 mmol), 1,4-ndc (10.8 mg, 0.05 mmol) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (29.1 mg, 0.1 mmol) were dissolved in 6 mL DMA- H_2O (1:1, v/v) mixed solvent and placed in a 25 mL polytetrafluoroethylene autoclave. After heating at 100 °C for 3 days, the reactor is naturally cooled to room temperature to obtain brown crystal, and the resulting product was washed 3 times with methanol. Elemental analysis: anal. calcd for $\text{C}_{58}\text{H}_{25}\text{N}_7\text{O}_{16}\text{Co}_3$: C 55.59; H 2.00; N 7.83%. Found: C 55.36; H 1.87; N 7.54%. IR (KBr, cm^{-1}): 980.48 (w), 1211.78 (w), 1255.98 (w), 1616.20 (w), 507.09 (m), 988.73 (m), 1050.83 (m), 1157.73 (m), 1318.08 (m), 1576.68 (m), 639.74 (s), 795.37 (s), 1371.53 (s), 1511.44 (s). CCDC-2082159 (Co-MOF) contains the supplementary crystallographic data for this paper.

Synthesis of Co/CoO@NC. Put the **Co-MOF** into the alumina crucible, and then move them to the tube furnace. The heat treatment was carried out in a flowing nitrogen atmosphere with the heating rate is 5 °C/min, and keep at 550 °C for 5 h. At last, it is naturally cooled to room temperature to obtain Co/CoO@NC hybrid material.

Catalytic reduction of 4-NP.

Add 0.2 mL 4-NP solution (2.5 mM), 2.5 mL distilled water, and 0.2 mL freshly prepared NaBH₄ aqueous solution (0.2 M) to the cuvette in order. Move the cuvette into JASCO V-770 UV-Vis spectrometer and set the test temperature. Drop 0.1 mL catalyst/water dispersions of various concentrations to start the reaction after the temperature stabilizes, and record the characteristic absorbance changes at different times.

3. Characterizations and results

Table S1 Crystallographic data of **Co-MOF**.

Compound	Co-MOF
Empirical formula	C ₅₇ H ₁₂ Co ₃ N ₆ O ₁₃
Formula weight	1165.56
Temperature/K	295.15
Crystal system	hexagonal
Space group	P6 ₃ /mmc
a/Å	16.866(7)
b/Å	16.866(7)
c/Å	15.377(6)
α/°	90
β/°	90
γ/°	120
Volume/Å ³	3788(3)
Z	1.99992
F(000)	1162.0
2θ range for data collection/°	4.83 to 50.2
Index ranges	-20 ≤ h ≤ 19, -19 ≤ k ≤ 20, -18 ≤ l ≤ 18
Reflections collected	26343
Data/restraints/parameters	1300/126/116
Independent reflections	R _{int} = 0.0423, R _{sigma} = 0.0156
Goodness-of-fit on F ²	1.150
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0710, wR ₂ = 0.2025
Final R indexes [all data]	R ₁ = 0.0758, wR ₂ = 0.2085

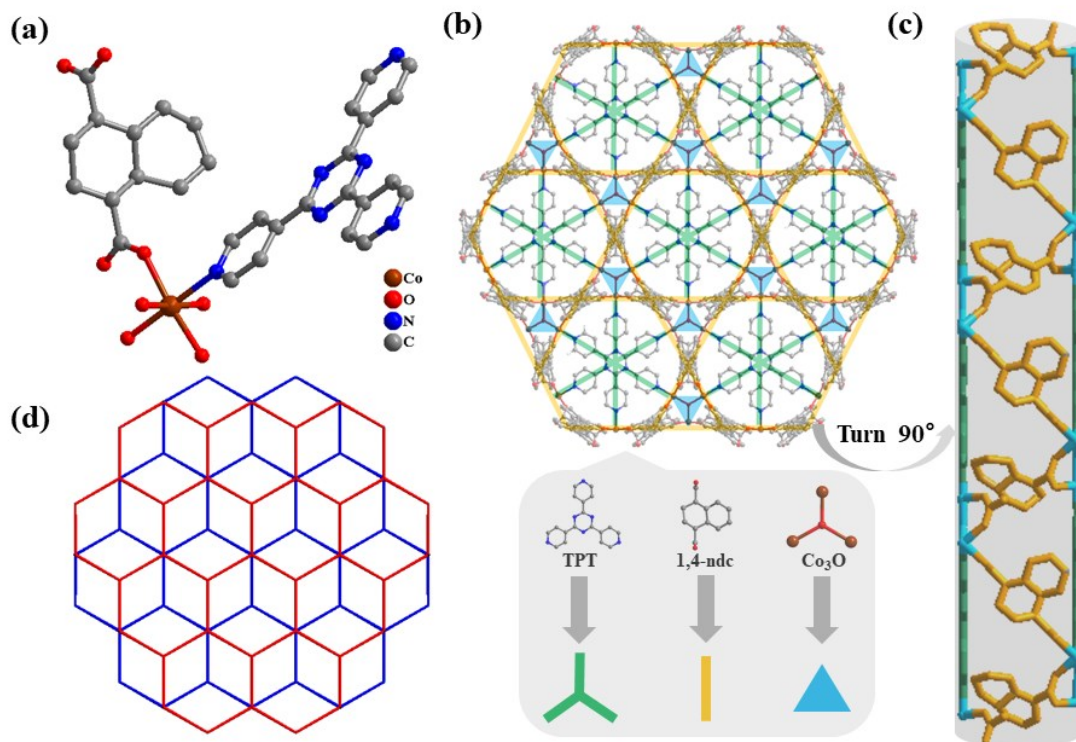


Fig. S1 (a) The coordination environment of Co (II); (b) 3D structure diagram of **Co-MOF**; (c) The connection between the 2D planes of **Co-MOF**; (d) Topological diagram of **Co-MOF**.

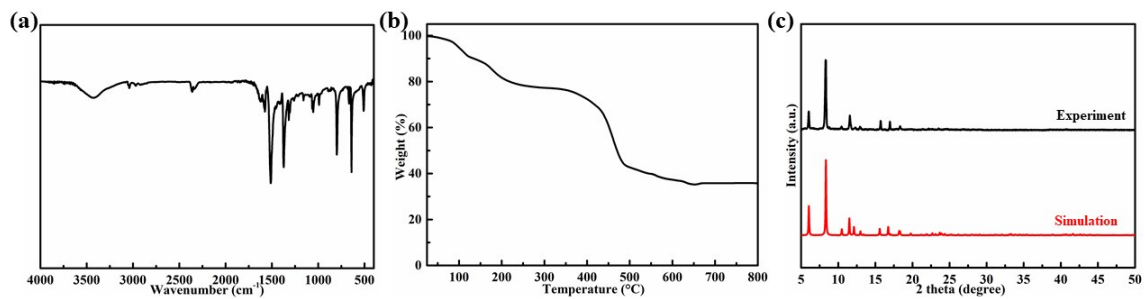


Fig. S2 (a) FTIR spectra, (b) TGA curves pattern and (c) experimental and simulation XRD of **Co-MOF**.

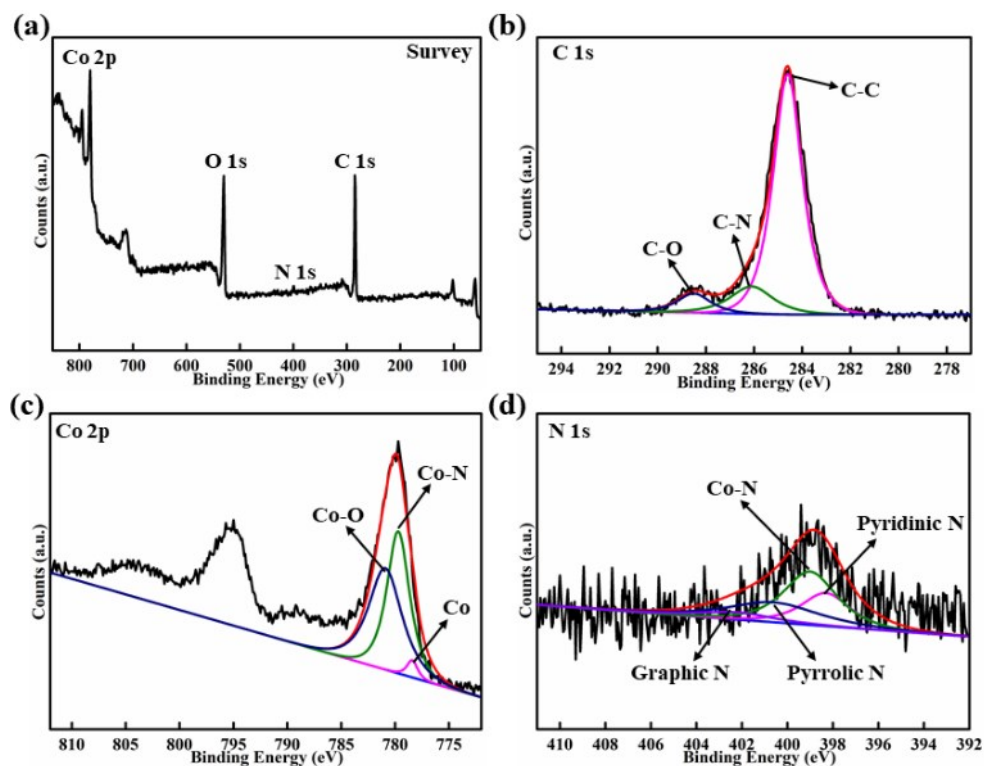


Fig. S3 XPS analysis of Co/CoO@NC: (a) full spectra; High-resolution spectrum of (b) C 1s, (c) Co 2p and (d) N 1s.

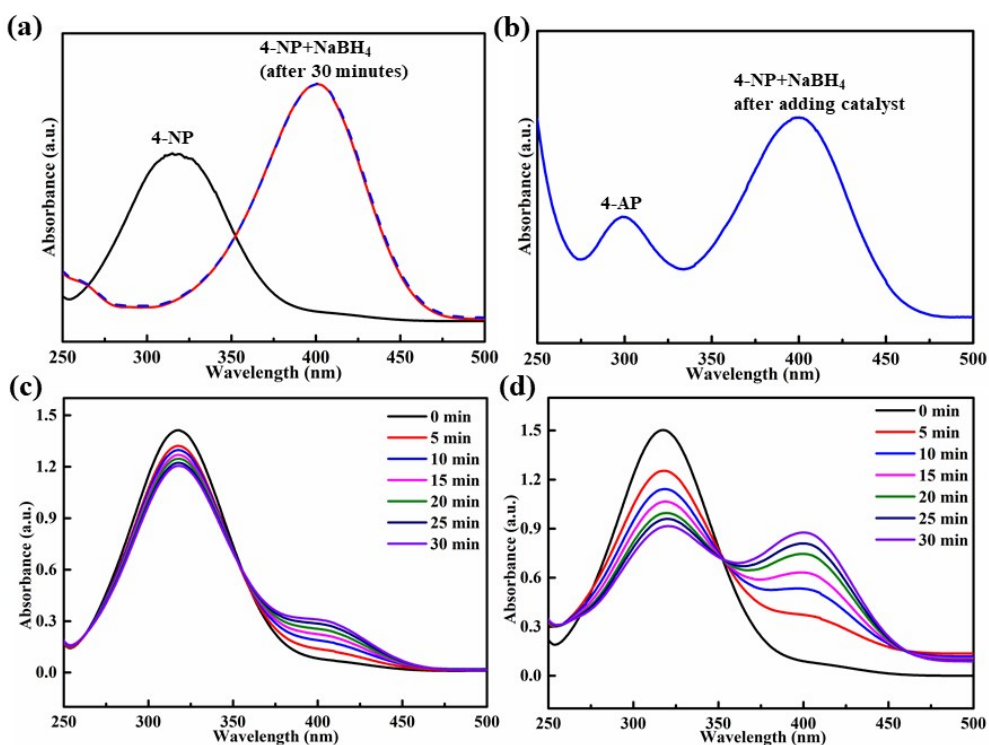


Fig. S4 (a) Absorption peak of 4-NP (black) and after adding NaBH_4 (red); (b) Absorption peak of 4-AP after adding catalyst; UV-vis spectrum with only (c) 0.1 mg and (d) 1 mg catalyst added.

Table S2 Comparison of 4-NP reduction rate between Co/CoO@NC and some precious metal catalysts.

Catalyst	Concentration of 4-NP ^a (mmol/L)	Amount of catalyst ^b (mg)	Rate constant (s ⁻¹)	References
Au/Fe ₃ O ₄ @SiO ₂	0.12	0.07	0.0013	18 (a)
Pt ₃ Au ₁ -PDA/RGO	0.09	0.06	0.0096	18 (b)
Ag ₂₀ Ni ₈₀ @CeO ₂	0.08	1.20	0.0110	18 (c)
Fe@SiO ₂ /Au ₂₅ Pt ₇₅	0.20	0.30	0.0130	18 (d)
Co/CoO@NC	0.17	0.20	0.0139	this work

^a The total 4-NP concentration of the reaction system.

^b Average dosage of 3.0 mL 4-NP solution.

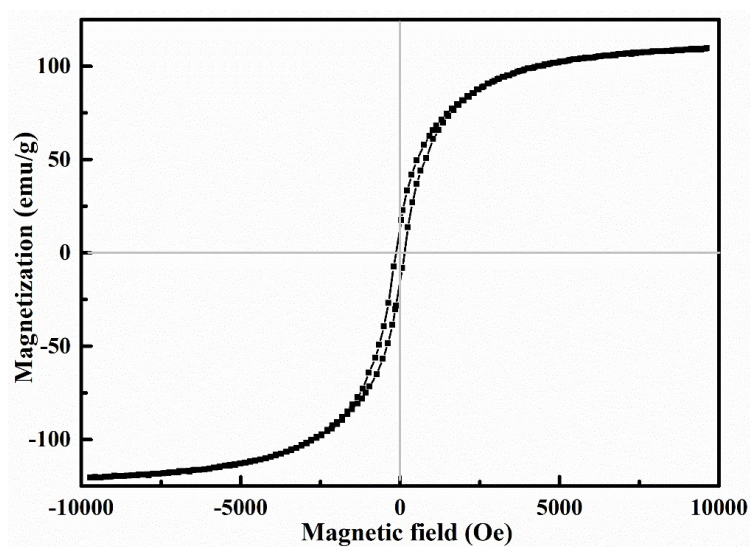


Fig. S5 Magnetic hysteresis loop of Co/CoO@NC (298 K).

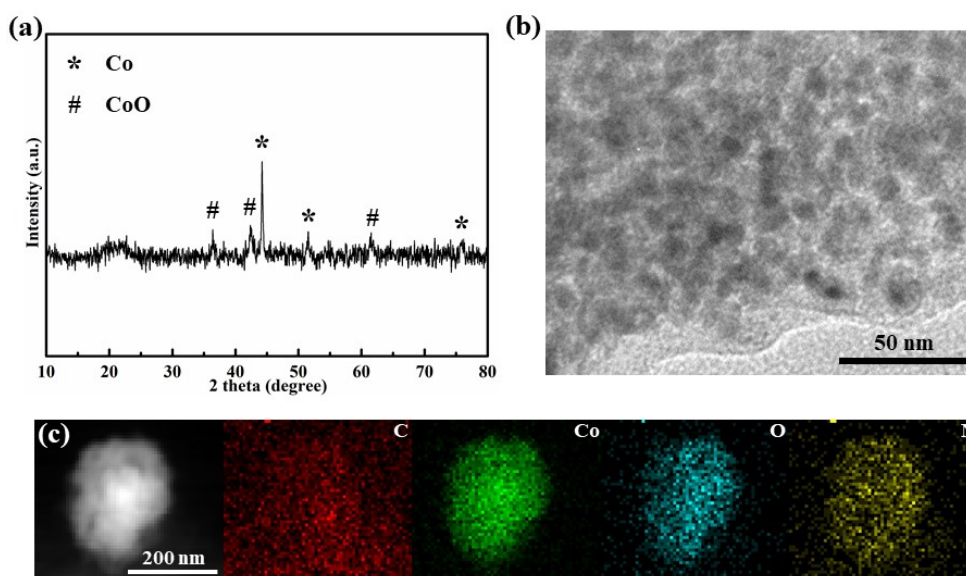


Fig. S6 (a) XRD curve, (b) TEM picture and (c) EDX elemental mapping of Co/CoO@NC after five cycles experiment.