Supplementary Information (SI) for Green Chemistry.

Supporting Information

Ammonium-Salt-Assisted Post Loading: A Cost-Effective Route to High-Performance Co–N–C with Enriched Active Sites in Surface for Nitroarene Hydrogenation

1.Experimental section

1.1 General Information

Cobalt(II) chloride hexahydrate ($CoCl_2·6H_2O$) and melamine ($C_3H_6N_6$) were purchased from Innochem. Ammonium salt was obtained from Aladdin, and nitric acid from McLean. Methanol for chromatography was purchased from Energy Chemicals, ethanol from Aladdin, and activated carbon was supplied by Sinopec Catalyst Co., Ltd. All nitro substrates were purchased from chemical companies, including Aladdin, Innochem, Sigma-Aldrich, and Energy Chemicals. All experiments used deionized water. All chemicals were of analytical grade and used directly without further purification.

1.2 Catalyst Characterization

X-ray diffraction (XRD) data were collected on a Rigaku Ultima IV diffractometer with Cu Ka (k = 1.5418 Å) radiation (50 kV, 40 mA) (Rigaku, Japan). X-ray photoelectron spectra (XPS) were recorded on a Thermo Scientific K-Alpha+ system (Thermo Scientific, USA). Transmission electron microscopy (TEM) images were obtained with an instrument FEI Talos F200S (FEI, USA). N_2 adsorption-desorption isotherms were measured by static N_2 physisorption at 77 K with a Micromeritics ASAP 2020 surface area and porosity analyzer (Micromeritics, USA). Raman spectra were measured by using a confocal Raman microscope (Renishaw, UK) equipped with a He-Ne laser (λ = 532 nm). Elemental contents are measured on an AVIO 200 (Perkin Elmer, USA) using inductively coupled plasma optical emission spectrometry (ICP-OES). The conversion and selectivity of the hydrogenation reaction of nitro compounds were determined by high-performance liquid chromatography (HPLC) (Shimadzu, LC-20AD, C18 column) and gas chromatography (GC) (FID detector, GC9790PLUS, crosslinked capillary HP-5 column). The X-ray absorption fine structure (XAFS) spectra (Co K-edge) and X-ray absorption near edge structure (XANES) spectra (Co K-edge) were obtained at beamline BL01C1 at the National Synchrotron Radiation Research Center (NSRRC), Taiwan. Co foil and CoO were used as reference samples. The data was analyzed with Athena and Artemis and included in the Demeter package.

1.3 Catalytic performance test

The hydrogenation performance of the catalyst is evaluated in a Teflon-lined stainless-steel autoclave. A specific quantity of nitro compounds, reaction solvents, and catalysts is introduced into the reactor. Subsequently, the reactor is purged with high-purity hydrogen and then pressurized to a predetermined level. The resulting products are then analyzed using HPLC or GC.

The conversion (Con.) and selectivity (Sel.) are defined as follows.

$$\text{Con.} = \frac{\text{moles of substrate reacted}}{\text{moles of substrate}} \times 100 \qquad \text{(S1)}$$

$$\text{Sel.} = \frac{\text{moles of aniline}}{\text{moles of substrate reacted}} \times 100 \qquad \text{(S2)}$$

General procedure for the hydrogenation of nitroarenes: Substrate (1.26 mmol), catalysts (20 mg), 10 ml of MeOH/H_2O (V:V, 19:1) were added into a 50 ml Teflon-lined stainless autoclave. The mixture was heated to 80 °C under 5 bar H_2 pressure. After 1.5-3 h, the reactant filtrate was analyzed by HPLC or GC.

Procedure for catalyst recycling: A catalyst (200 mg), p-chloronitrobenzene (12.6 mmol), and 200 mL of a MeOH/H_2O (V:V, 19:1) were placed in a 500 mL autoclave. The reaction was carried out at 110 °C under 10 bar of H_2 for 2 hours. Upon completion, the catalyst was separated by centrifugation, washed with alcohol, and dried under a vacuum to prepare it for further testing.

Procedure for catalyst regeneration: The catalyst was treated at 500 °C under a H_2/Ar atmosphere (10% H2 by volume) for 1 hour.

H-D isotope dynamics evaluation: Kinetic isotope effects were studied using nitrobenzene hydrogenation as a model reaction, with H_2 or D_2 as hydrogen donors. The amount of Co/NC-AM catalyst was kept at 20 mg, keeping H_2/D_2 pressure of 5 bar, and the reactants were detected by High-performance liquid chromatography (HPLC).

1.4 Cost Accounting

The detailed cost calculation per ton of catalyst is as follows: Raw-material cost for Co/NC-AM. According to market research, the prices of cobalt(II) chloride hexahydrate ($CoCl_2·6H_2O$), Ammonium-Salt, activated carbon (C), melamine ($C_3H_6N_6$) are \$6320 t^{-1}, \$702 t^{-1}, \$2809 t^{-1}, \$562 t^{-1}, and \$562 t^{-1}, respectively. The yield for preparing NC from activated carbon and melamine is 50%, while the yield for loading $CoCl_2·6H_2O$ onto NC is 76%.

2. Figures and tables

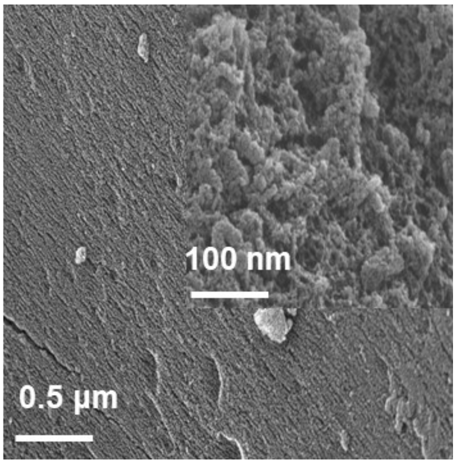


Figure S1. SEM of Co/NC-AM.

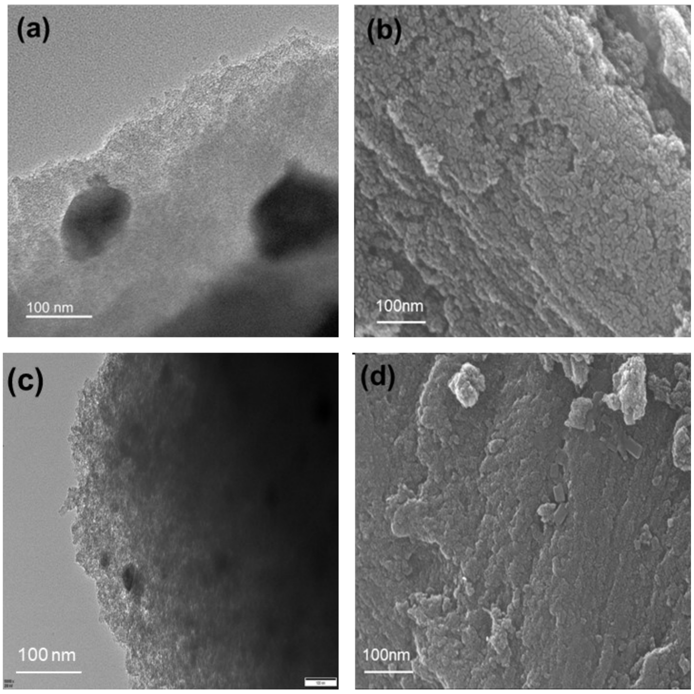


Figure S2. (a) TEM and (b) SEM of Co/NC-ISP; (c) TEM and (d) SEM of Co/NC.

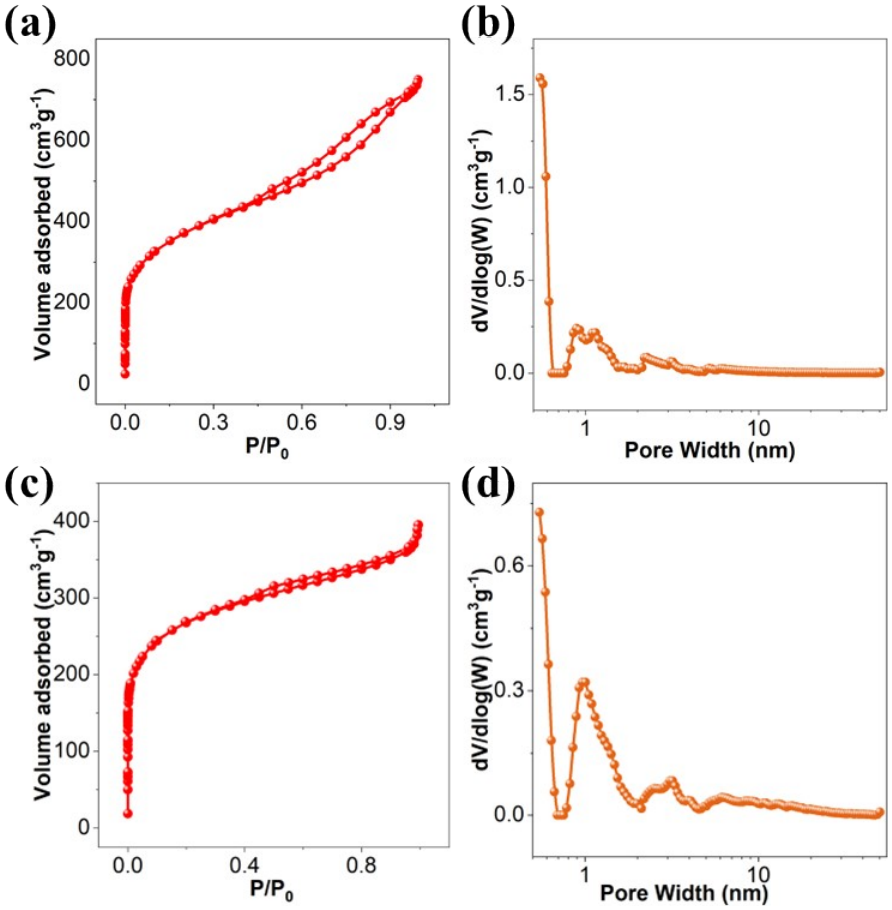


Figure S3. (a) N_2 sorption isotherms and (b) pore size distributions of Co/NC; (c) N_2 sorption isotherms and (d) pore size distributions of Co/NC-AM.

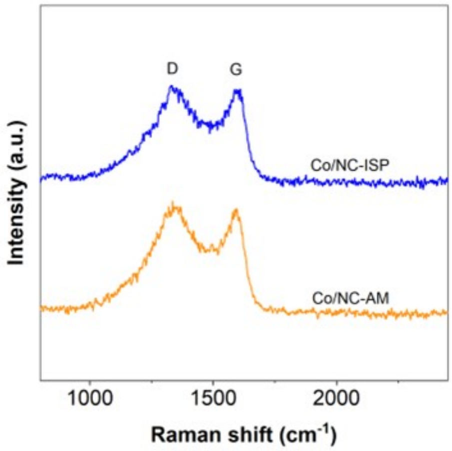


Figure S4. Raman spectra of different catalysts.

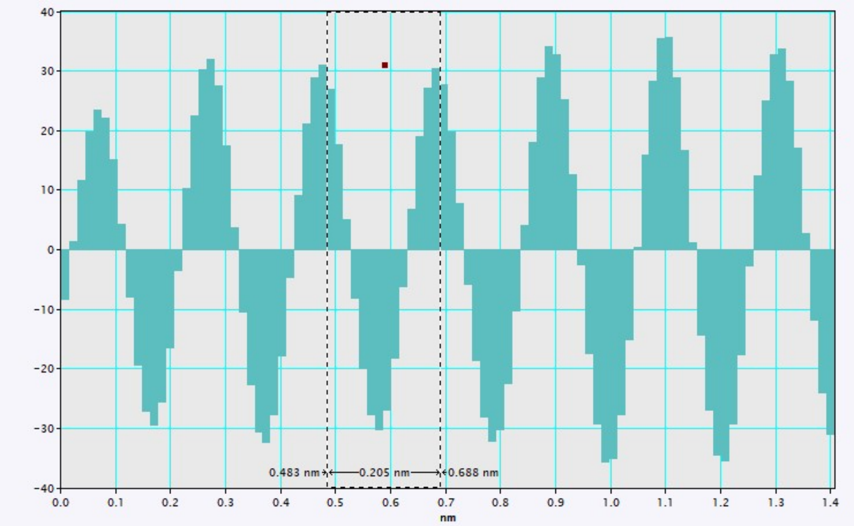


Figure S5. The lattice distance of Co/NC-AM processed from Digital Micrograph.

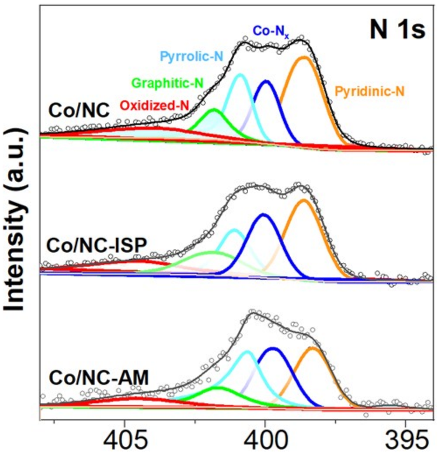


Figure S6. High-resolution N 1s XPS spectra of Co/NC-AM, Co/NC-ISP, and Co/NC-AM-AL catalysts.

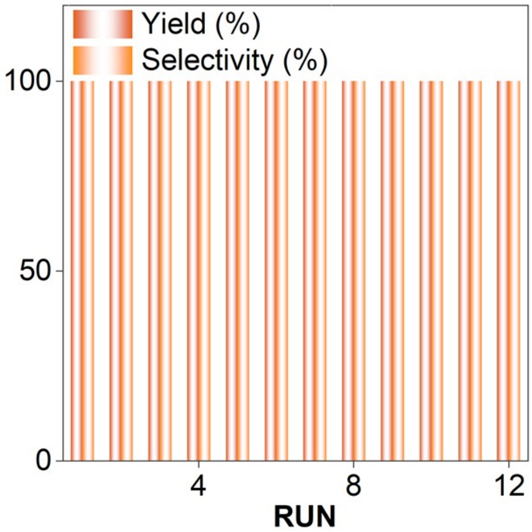


Figure S7. Recycling results of the Co/NC-AM catalyst. Reaction condition: 200 mg catalyst, 12.6 mmol nitrobenzene, 10 mL solvent(H_2O: MeOH=1:19,v/v), 110 °C, 10 bar H_2, 2 h.

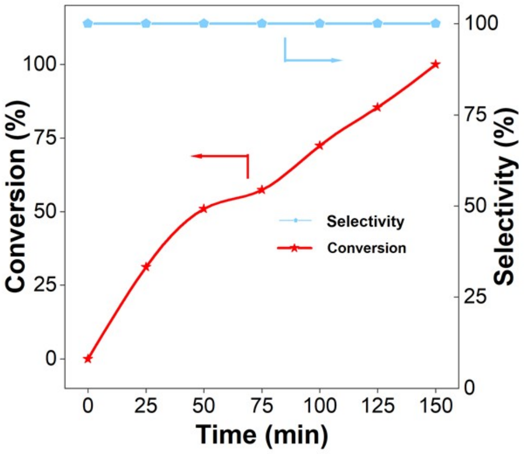


Figure S8. Kinetic curves of the Co/NC-AM catalyst. Reaction condition: 20 mg catalyst, 1.26 mmol nitrobenzene, 10 mL solvent (H_2O: MeOH=1:19,v/v), 80 °C, 5 bar H_2, 2.5 h.

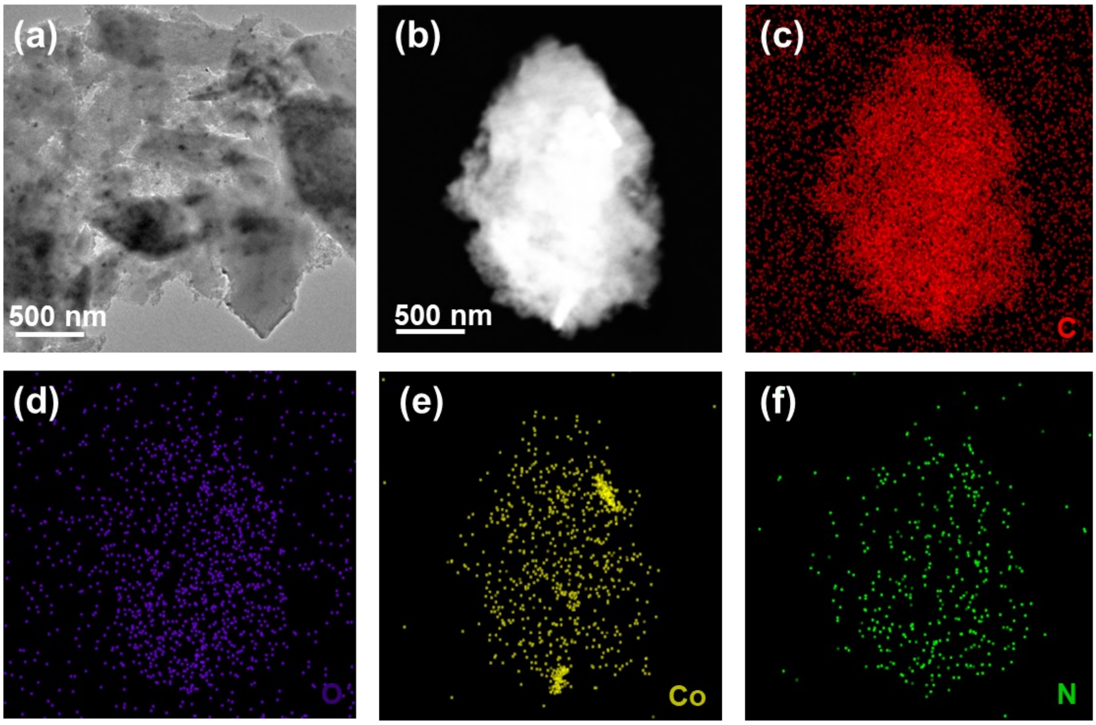


Figure S9.TEM images of the Co/NC-AM catalyst after cycling.

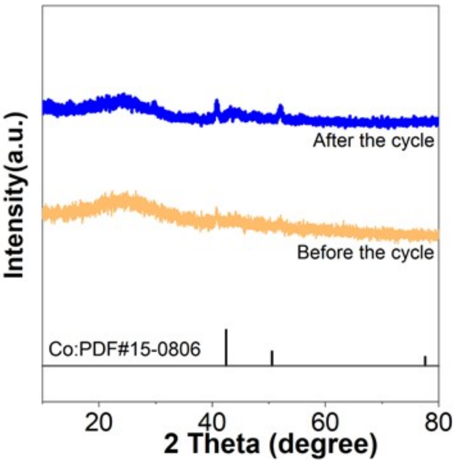


Figure S10. XRD patterns of the Co/NC-AM catalyst before and after cycling.

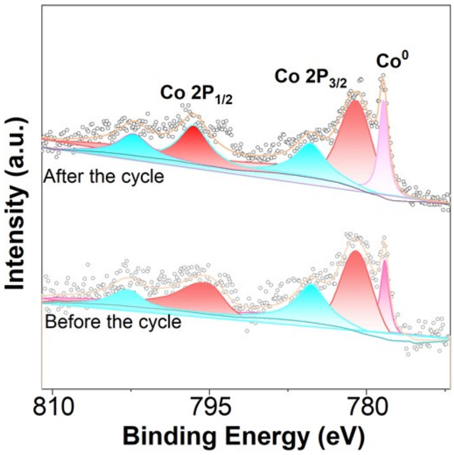


Figure S11. XPS patterns of the Co/NC-AM catalyst before and after cycling

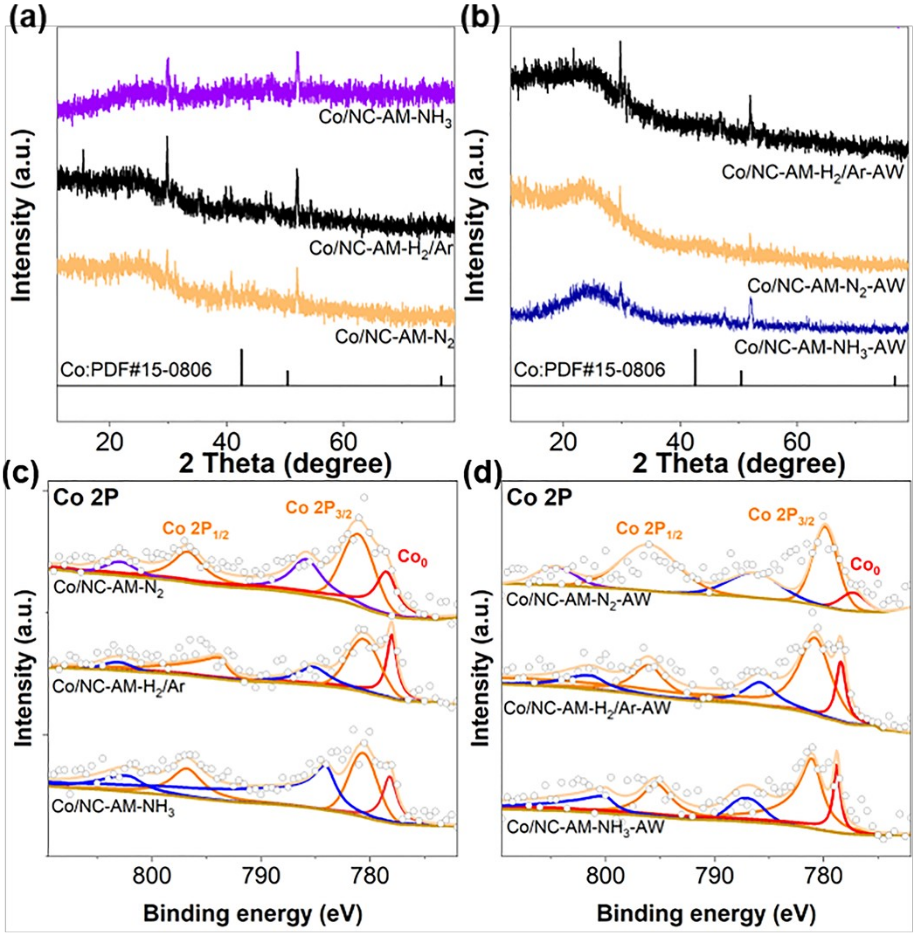


Figure S12. (a) and (b) XRD patterns of catalysts prepared under different atmospheres. (c) and (d) XPS patterns of catalysts prepared under different atmospheres.

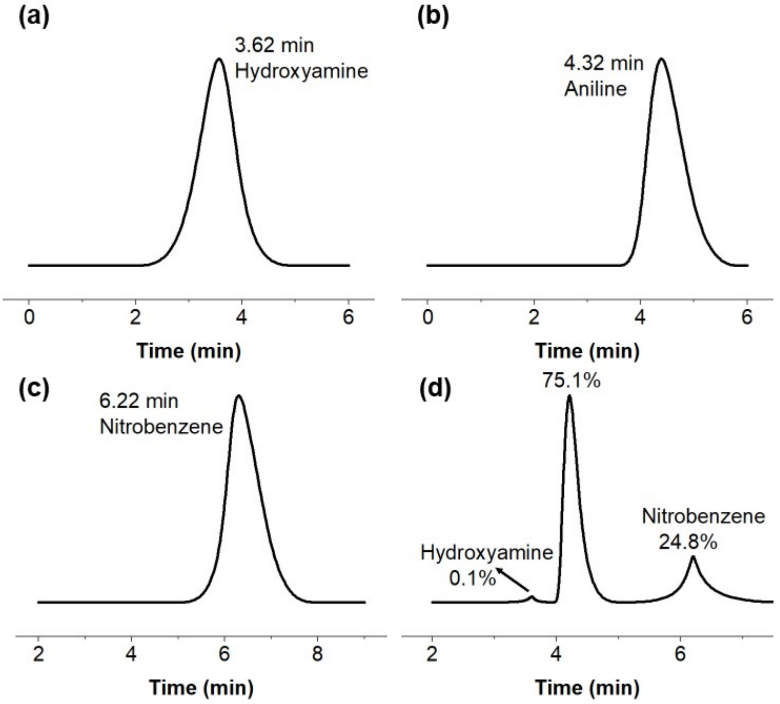


Figure S13. (a) Hydroxylamine detection chromatogram obtained by gas chromatography;(b) Aniline detection chromatogram obtained by gas chromatography; (c) Nitrobenzene detection chromatogram obtained by gas chromatography; (d) GC chromatogram of the products from nitrobenzene hydrogenation catalyzed by Co/NC-AM.

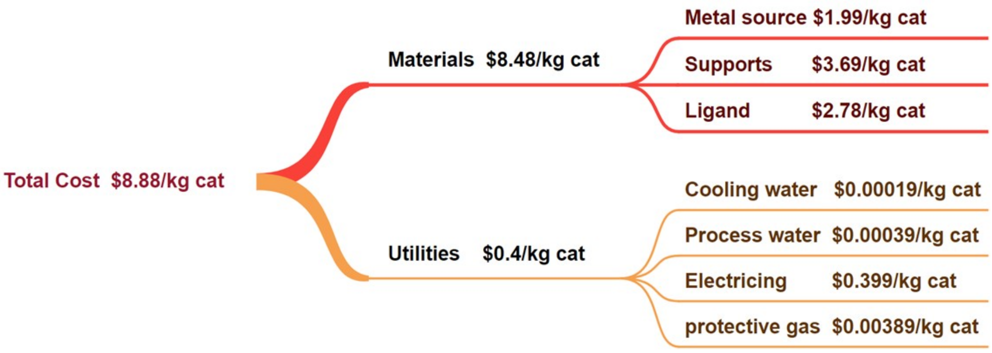


Figure S14. Cost Accounting by “CatCost”.

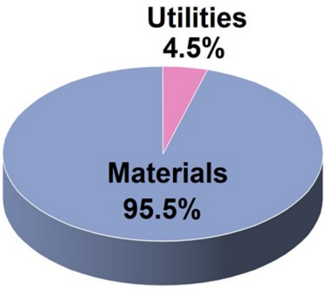


Figure S15. Preparation cost proportion of the kilogram-scale catalyst.

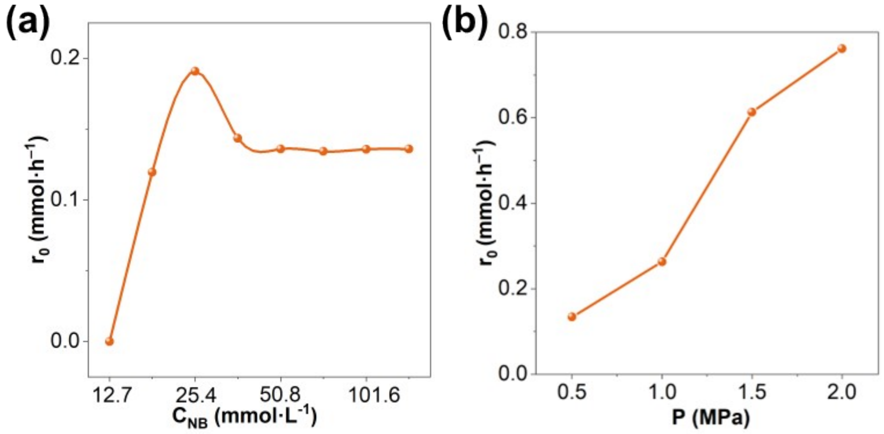


Figure S16. Rate-limiting steps in the hydrogenation of nitrobenzene:(a) reaction rate vs. substrate concentration;(b) reation rate vs. hydrogen pressure.

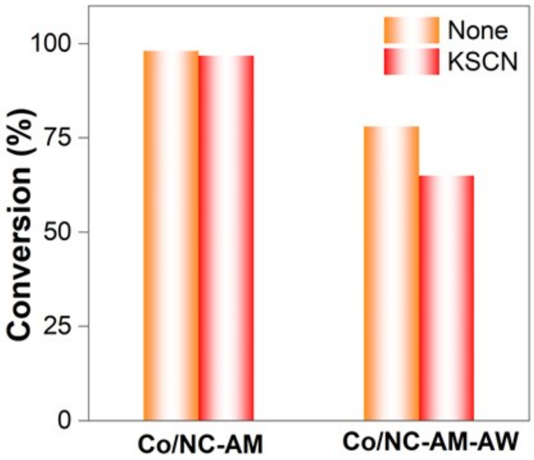


Figure S17. The influence of KSCN on the catalytic performance of Co/NC-AM and Co/NC-AM-AW.

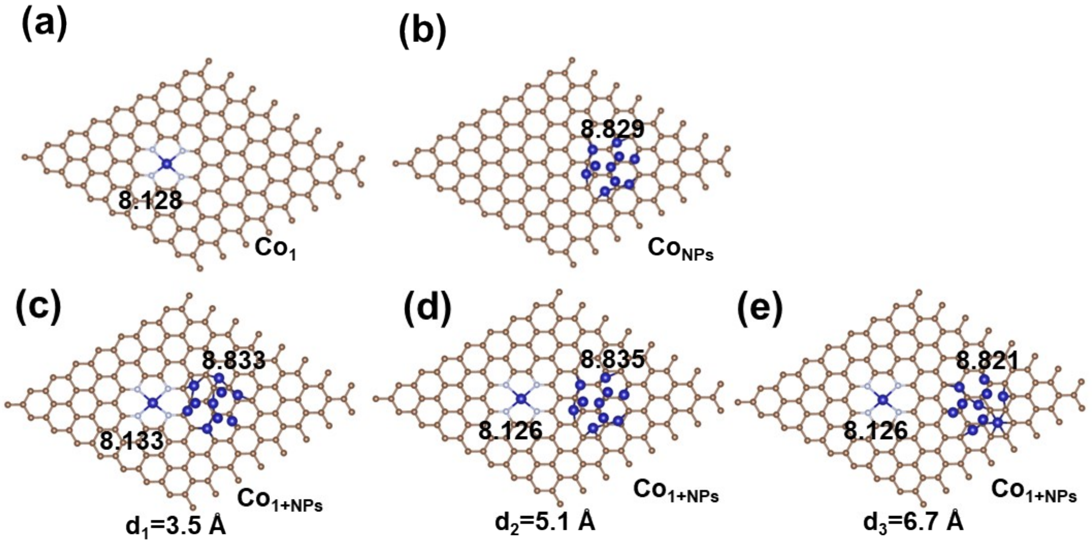


Figure S18. Schematic charge-density distributions for models with varying separations between single-atom sites (Co_1) and nanoparticles (Co_{NPs}). (a) Co_1 site model; (b) Co_{NPs} model; (c-e) Co_{1+NPs} model with different distance.

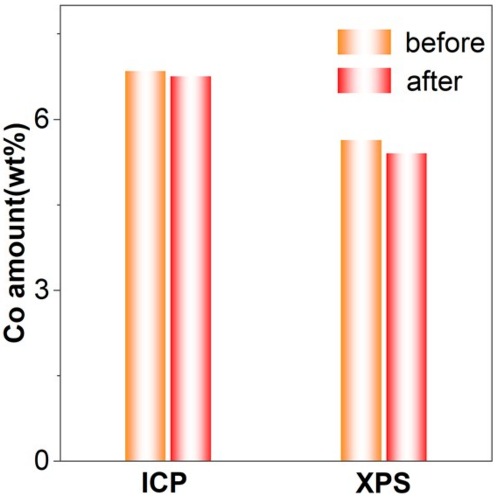


Figure S19. Changes in XPS and ICP of Co/NC-AM before and after ball milling.

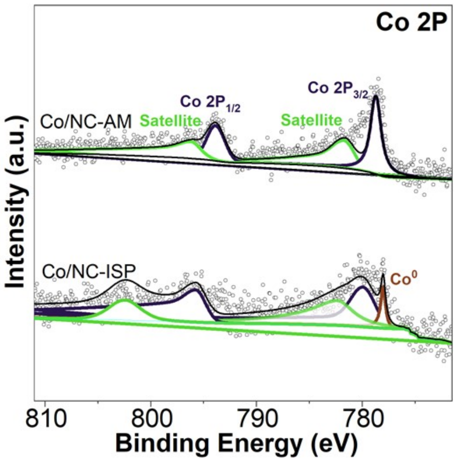


Figure S20. High-resolution Co 2p XPS spectra of the acid-washed Co/NC-AM and Co/NC-ISP catalysts.

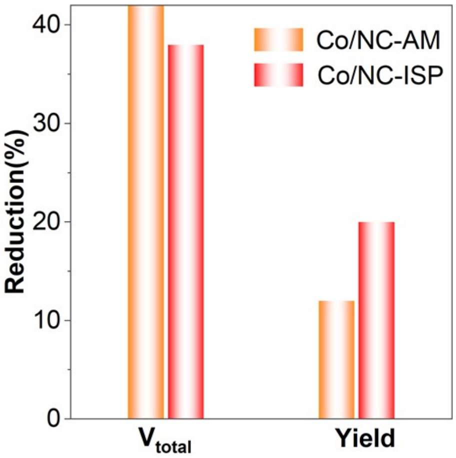


Figure S21. Reduction in catalyst yield and pore volume after cycling.

Table S1. Summary of surface areas and pore volumes for all samples.

Sample	S_{BET} [a] (m^2·g^{-1})	S_{micro} [b] (m^2·g^{-1})	V_{total} [c] (cm^3·g^{-1})	V_{micro} [d] (cm^3·g^{-1})
Co/NC-AM	1200.00	770.00	0.94800	0.29500
Co/NC-ISP	1026.90	697.87	0.54348	0.28118
Co/NC-AM-5th	633.97	356.01	0.54995	0.15675
Co/NC-ISP-5th	539.92	387.71	0.33615	0.14802
Co/NC	1001.60	772.91	0.52342	0.27540

Note: [a] Calculated surface area using the BET model; [b] Cumulative micropore surface using t-Plot model; [c] V_{total}: total volume calculated at P/P_0 = 0.99; [d] V_{micro}: micropore volume calculated from t-Plot model.

Table S2. Summary of XPS results for all samples.

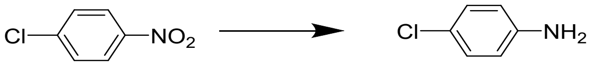
Sample	C	N	O	Co
Co/NC-AM	86.96	5.81	5.99	1.24
Co/NC-ISP	85.50	6.54	7.10	0.87
Co/NC	88.44	5.43	5.52	0.60

Note: All data are given in atomic%.

Table S3. EXAFS fitting parameters at the Fe *K*-edge for various samples (S_0^2 = 1).

Sample	Shell	*CN*	*R*(Å)	σ^2 (10^{-4} Å^2)	ΔE_0(eV)	*R* factor
Co foil	Co-Co	12.01	2.48	0.0024	7.05	0.00072
Co/NC-AM-AW	Co-N	3.16	1.958	0.0074	-0.391	0.00721

Table S4. Catalytic hydrogenation of 1-chlor-4-nitrobenzene over various catalysts under different reaction conditions.



Entry	Catalyst	T (°C)	H_2 (bar)	Con. (%)	Sel. (%)
1	Co/NC	60	5	30	0
2	Co/NC-AM	60	5	50	99.9
3	Co/NC- $(NH_4)_2CO_3$	60	5	35.5	99.9
4	Co/NC- NH_4HCO_3	60	5	31.2	99.9
5	Co/NC- NH_4Cl	60	5	34.7	99.9
6	Co/NC- NH_4OAc	60	5	42.2	99.9

Reaction conditions:1.27mmol substrate; 20mg catal;0.5ml H_2O; 9.5ml MeOH;3 h.

Table S5. The Co contents in different samples as a function of etching time were determined by XPS.

Time(s)	Co contents (Atomic %)[a]
0	0.89
20	0.57
40	0.86
60	0.46

a: The data were obtained for Co/NC-AM-AW by XPS analysis;

Table S6. Catalytic hydrogenation of nitrobenzene over our proposed Co_1/CoNPs@CNT catalysts and recently documented catalysts.

Catalyst	Solvent	P_{H2} (Mpa)	T(℃)	Time(h)	Con.(%)	Sel.(%)	Ratio (mmol/mg)	Ref.
Co/NC-AM	**MeOH/H_2O**	**0.5**	**80**	**3**	**>99**	**>99**	**1.28/20**	**This work**
Co-DABCO-TPA@C-800	T-BuOH	4	120	2	92	92	0.35/10	Sci. China Mater., 2017, 60, 1269
Co-N-C	NaOH/t-BuOH	3	80	1.5	97	97	0.7/20	Chem. Sci., 2016, 7, 5758
Co@C NPs	THF	0.7	120	6	93	95	0.5/30	J. Catal., 2013, 340, 1
Co/Gs@C	t-BuOH	4	120	15	87	87	0.5/35	Nat Protoc., 2015, 15, 1313
Co-PZ-TPA@HAP-800	PrOH/H_2O	1	80	24	95	95	0.5/50	ChemCatChem, 2024, 16, e202301027
CoNC/CNT	MeOH	2	110	10	99.8	97.88	0.4/20	Catal. Sci. Technol., 2016, 6, 1007
CoNC/CNT-HCl	MeOH	2	110	12	100	87.78	0.4/20	Catal. Sci. Technol., 2016, 6, 1007
Co/CNT	fixed bed reactor		100	2	90	90	0.1/100	ACS. Catal., 2014, 4, 1478
Co-N-C	$N_2H_4 \cdot H_2O$/EtOH	0.4	80	60	32.4	32.4	0.5/10	Mol. Catal., 2020, 7, 497111226

Co-Co_3O_4/NGr@C	EtOH/H_2O	2	70	20	96	96	0.5/5	Catal. Sci. Technol., 2016, 6, 4473
Co@C-N	$N_2H_4\cdot H_2O$/EtOH	0.1	550	24	100	94	0.25/20	ACS Catal., 2013, 5, 1
75Co-phen@C-800-8M	i-PrOH	2	90	24	89	89	0.5/64	Chem Catal., 2022, 2, 178
Co_1/h-NC	EtOH	2	120	6	＞99	＞99	0.75/50	ACS Appl. Mater. Inter., 2020, 12, 17651
Co-0.05M	THF/H_2O	2	110	4	＞99	95	0.15/20	Org. Process Res. Dev., 2016, 20, 452
Co@N_1Gs-700	EtOH	2	200	6	99.9	94.7	0.5/20	Appl. Catal. B-Environ., 2020, 263, e118339
Co_3O_4-Phen@C	THF/H_2O	2.7	125	24	84	99	0.5/15	Org. Process Res. Dev., 2018, 22, 430
Co-terephthalic acid-piperazine@SiO_2-800	H_2O	1	50	16	99	94	0.5/25	ChemCatChem, 2022, 14, e202101234
Co-DABCO-TPA@C-800	BuOH	4	120	15	90	90	0.5/25	Science, 2017, 358, 326
Zn_4Co_1Ox@carbon particles	THF	5	70	2	99	＞99	0.2/30	Adv. Sci., 2019, 6, 1900807
Co@C NPs	toluene	0.4	25	2	100	＞99	1/50	Chem.Eur.J., 2023, 29, e202203142

Co-S-N	THF/H_2O	5	100	2	99	99	0.6/62	Chem. Select., 2020, 5, 7249
CoO_x@NCNTs	EtOH	3	110	3	>99	>99	1/40	ACS Catal., 2015, 5, 4783
Co-N-C	HCOOH	3	80	1.5	100	97	0.2/30	Appl. Catal. B-Environ., 2018, 227, 386
Co_1/NPC	EtOH	3	110	1.5	>99	>99	1/50	Nat. Commun., 2022, 13, 723
CoN_x-Co_yZnS@NPC-Z	MeOH/H_2O	0.5	90	3	100	99.9	0.25/20	J. Am. Chem. Soc., 2022, 144, 9280
$Co_{(6)}$-N-C	PhMe	3	80	3.7	96	99	0.5/50	Fuel, 2024, 375, 132567.
Co-N-C@SiO_2	EtOH	4	120	18	100	>99	0.5/40	ACS Appl. Mater. Inter., 2020, 12, 3624
Co/NPHC	EtOH	1	100	2	100	>99	0.5/10	Catal. Lett., 2023, 153, 824
Co_1-N/P-C	EtOH	2	100	2	99	>90	0.5/10	Appl. Catal. B-Environ., 2024, 346, 123762.
Co_3O_4/N-Gr/Fe_3O	EtOH	4	120	15	>99	>99	0.5/10	ACS Appl. Nano. Mater., 2021, 4, 3508

Co@NC-800	H_2O	1	100	14	>99	>99	0.5/30	Green Chem., 2021, 23, 4490
Co@NC-X	PhMe	3	80	2	99	99	0.5/50	Sci. China Mater., 2023, 66, 169
$Co/Zn_{1-1}@NC$	IPA	1	100	0.5	>99	>95	0.5/40	Mol. Catal., 2024, 555, 113911.
NiCo/SBA-16	$MeOH/H_2O$	1	80	3	98.7	95.9	1/10	ACS Omega., 2023, 8, 12339
TAHCF/Co-N	MeOH	2	85	3	>99	>99	0.125/10	Chem. Eng. J., 2024, 490, 151678.
$CoCorrPPh_3@Vulcan$-800	MeOH	4	120	16	>99	>99	0.25/12	ACS Catal., 2022, 12, 11
Co@NCG-800	IPA	1	100	2.5	100	99	1.23/50	New Carbon Mater., 2023, 38, 555
Co_1/NPC	$EtOH/H_2O$	3	110	3.5	100	>99	2/5	Nat. Commun., 2022, 13, 723
Co/C-PAQ	$EtOH/H_2O$	1	80	2	>99	>99	0.8/20	ACS Catal., 2022, 12, 11960
Co-N-CNS-Th	EtOH	2	100	1	99	99	0.5/10	J. Mater. Chem. A., 2022, 10, 9435
Co@NC/AC-800	MeOH	1	110	4	100	100	1/12	Cat. Lett., 2023, 153, 1536.

SA-Co/NSPC	MeOH/H_2O	2	120	6	100	>99	0.5/30	J. Catal., 2022, 414, 101
Co_1/NSC-AT	H_2O	0.5	35	3	>99	>99	0.25/20	ACS Catal., 2022, 12, 5786
Co-Nx/C-800-AT	H_2O	0.35	110	1.5	100	>99	1/40	Sci. Adv., 2017, 3, e1601945
CMK-3-CoPc	2-methyltetrahydrofuran	2	40	24	100	>99	0.5/30	Catal. Sci. Technol., 2019, 9, 157
CoN_x-OMCs	H_2O	0.5	110	1.5	100	>99	1/20	Nanoscale., 2018, 10, 16839
Co/MA-800	THF/H_2O	4	120	18	>99	>99	0.5/50	ACS Appl. Nano Mater., 2020,3, 11070
Co@NMC-800	EtOH	1	80	1.3	>99	>99	1/40	J. Catal., 2017, 348, 212
Co_1-N/P-C	EtOH	2	100	2	>99	>99	0.5/10	Chem. Eur. J., 2018, 24, 4234
CoO_x@NCNTs	EtOH	3	110	2.5	>99	98	1/20	ACS catal., 2015, 5, 4783
Co-CoO_x@N-C	THF/H_2O	5	70	2	>99	>99	0.2/10	Adv. Sci., 2019, 6, 1900807
Co-Co_3O_4 @SiO_2	MeOH	1.5	70	16	95	100	0.5/25	ChemCatChem, 2022, 14, 202101234

Table S7. Catalytic hydrogenation of *p*-CNB under various solvent conditions.

Entry	Catalyst	Solvent	T (°C)	H_2 (bar)	t (h)	Con.(%)	Sel.(%)
1	Co/NC-AM	H_2O	90	10	2	67.9	46.8
2	Co/NC-AM	MeOH	90	10	2	31.7	99.9
3	Co/NC-AM	EtOH	90	10	2	43.4	99.9
4	Co/NC-AM	EA	90	10	2	4.8	99.9
5	Co/NC-AM	EtOH/H_2O (19/1, V/V)	90	10	2	71.3	99.9
6	Co/NC-AM	MeOH/H_2O (19/1, V/V)	90	10	2	99.9	99.9
7	Co/NC-AM	THF	90	10	2	10	99.9

Reaction conditions:0.38 mmol *p*-CNB in 10 mL of solvent by using 20 mg of a catalyst.

Table S8. Catalytic hydrogenation of p-CNB.

Entry	Catalyst	Con.(%)	Sel.(%)
1	Co/NC-AM-Ar	50.0	>99
2	Co/NC-AM-N_2	49.5	>99
3	Co/NC-AM-H_2/Ar	20.6	>99
4	Co/NC-AM-NH_3	33.5	>99

Reaction conditions:1.27mmol substrate; 20mg catal;0.5ml H_2O; 9.5ml MeOH;3 h,60℃.

Table S9. The Co contents in different samples were determined by ICP.

Entry	Catalyst	Co contents(wt%)
1	Co/NC-AM-Ar	6.85
2	Co/NC-AM-Ar-AW	1.22
3	Co/NC-AM-N_2	6.64%
4	Co/NC-AM-N_2-AW	1.23%
5	Co/NC-AM-H_2/Ar	8.6%
6	Co/NC-AM-H_2/Ar-AW	4.3%
7	Co/NC-AM-NH_3	10.8%
8	Co/NC-AM-NH_3-AW	3.3%

Table S10. Catalytic Hydrogenation of p-CNB Using Different Hydrogen Sources

Entry	Hydrogen Sources	T (℃)	t (h)	Con.(%)	Sel.(%)
1	HCOOH	110	3	76.9	99.9
2	$NaBH_4$	110	3	99.9	99.9
3	CH_3OH	110	3	15.8	99.9
4	C_6H_8Si	110	3	99.2	99.9

Reaction conditions:1.26 mmol p-CNB ;20mg catalyst; 0.5ml H_2O; 9.5ml MeOH.

Table S11. The Co contents in different samples were determined by ICP.

Entry	Catalyst	Co contents(wt%)
1	fresh catalyst	6.85
2	recycled catalyst	6.76