

## *Electronic Supplementary Information*

### **“Trojan Horse” Strategy Towards Robust Co-N<sub>4</sub> Active Sites Accommodated in Micropore Defect-Rich Carbon Nanosheets for Boosting Selective Hydrogenation of Nitroarenes**

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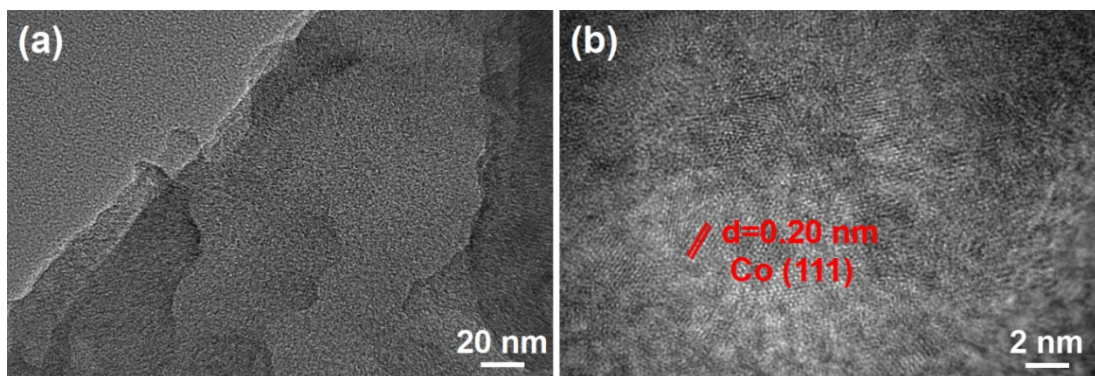
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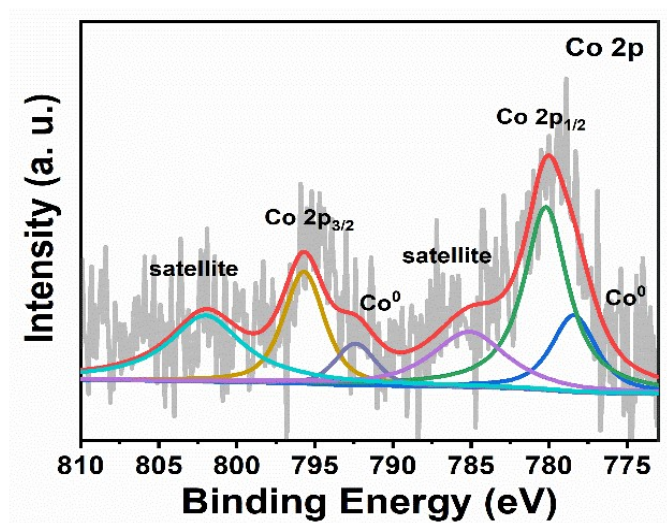
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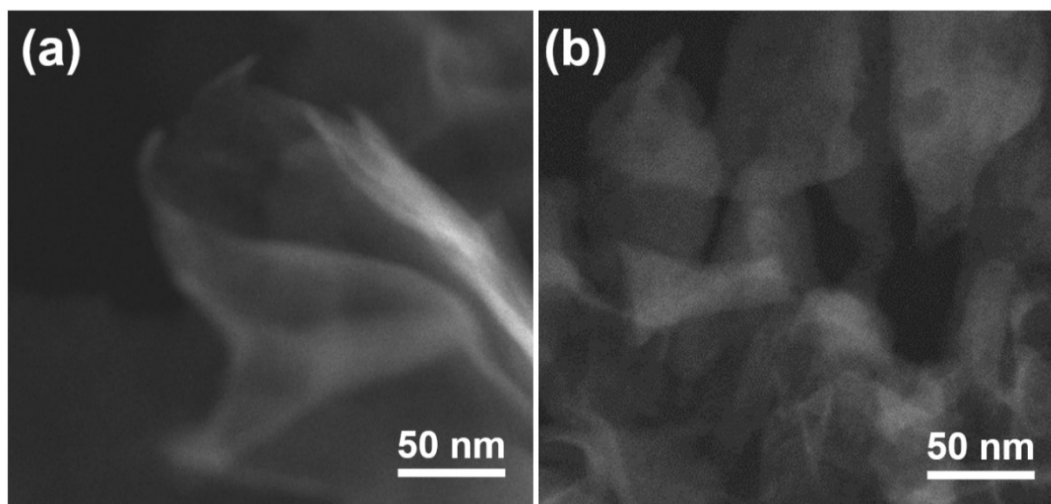
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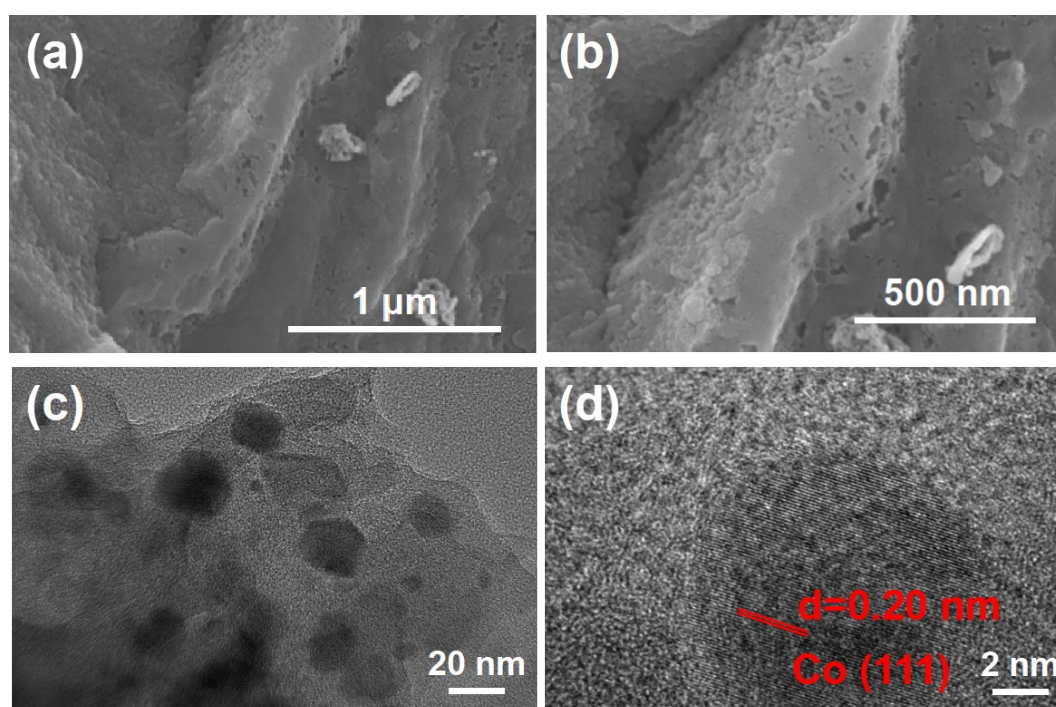
**Fig. S1** TEM images of Co-N-CNS-Th-u (Co-N-CNS-Th-u was prepared through the same procedures with Co-N-CNS-Th except for HCl washing).



**Fig. S2** Co 2p XPS spectrum of Co-N-CNS-Th-u.



**Fig. S3** TEM images of CNS and Co-N-CNS.



**Fig. S4** (a, b) SEM and (c, d) TEM images of Co-N-C.

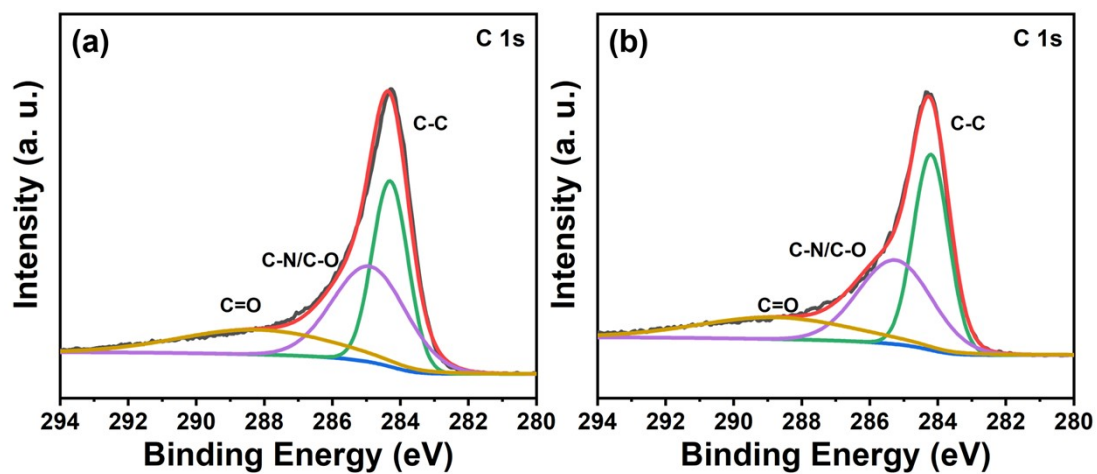


Fig. S5 C 1s XPS spectra of (a) Co-N-CNS-Th and (b) Co-N-CNS.

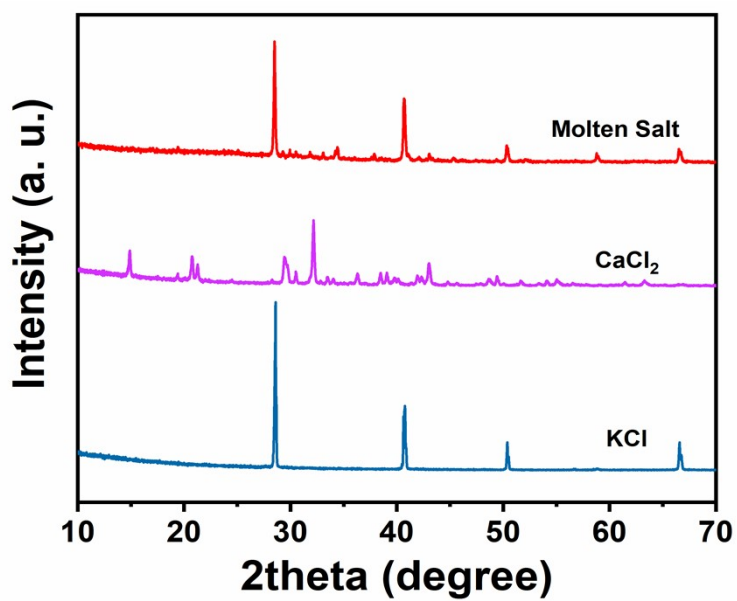
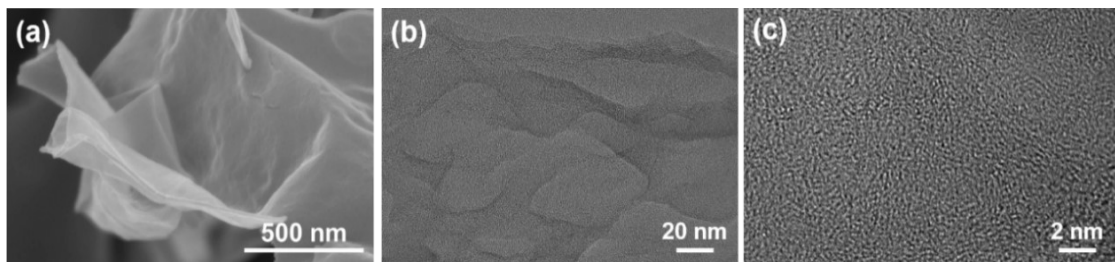
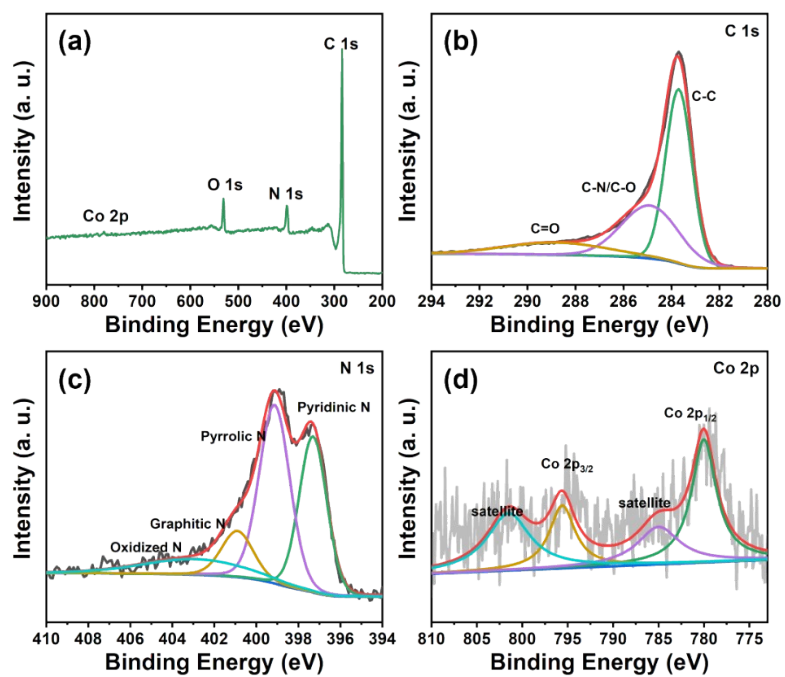


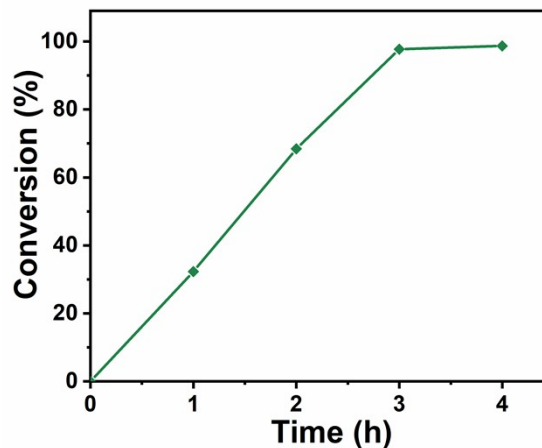
Fig. S6 XRD patterns of the recovered molten salt, KCl, and CaCl<sub>2</sub>.



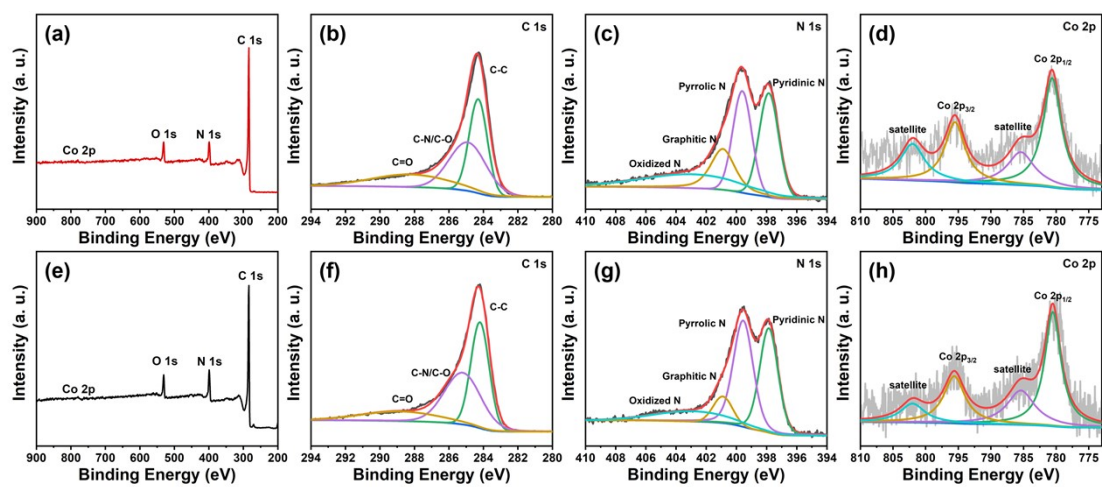
**Fig. S7** (a) SEM and (b, c) TEM images of Co-N-CNS-Th-r.



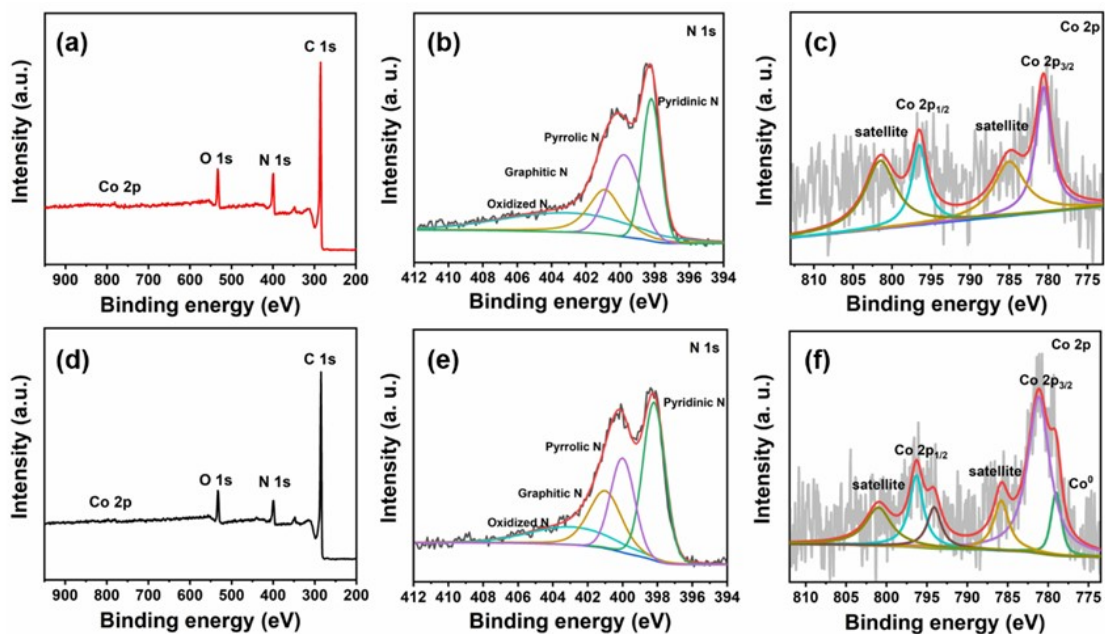
**Fig. S8** (a) XPS survey spectrum, (b) C 1s XPS spectrum, (c) N 1s XPS spectrum, and (d) Co 2p XPS spectrum of Co-N-CNS-r.



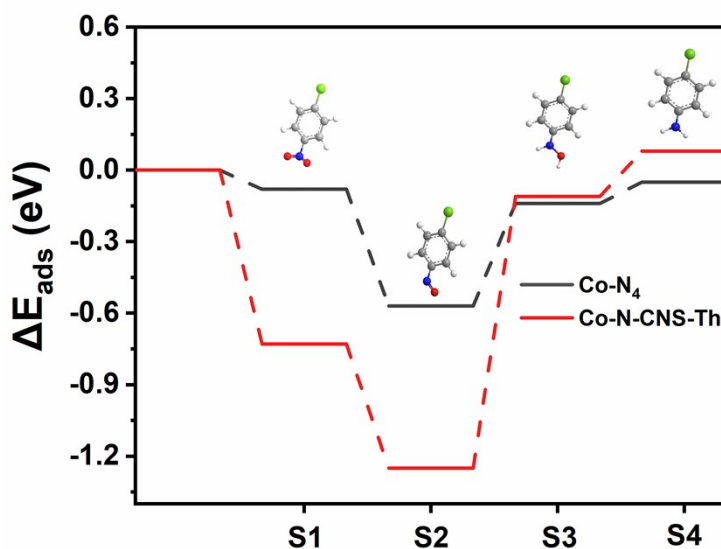
**Fig. S9** Time-dependent catalytic performance of Co-N-CNS-Th-k.



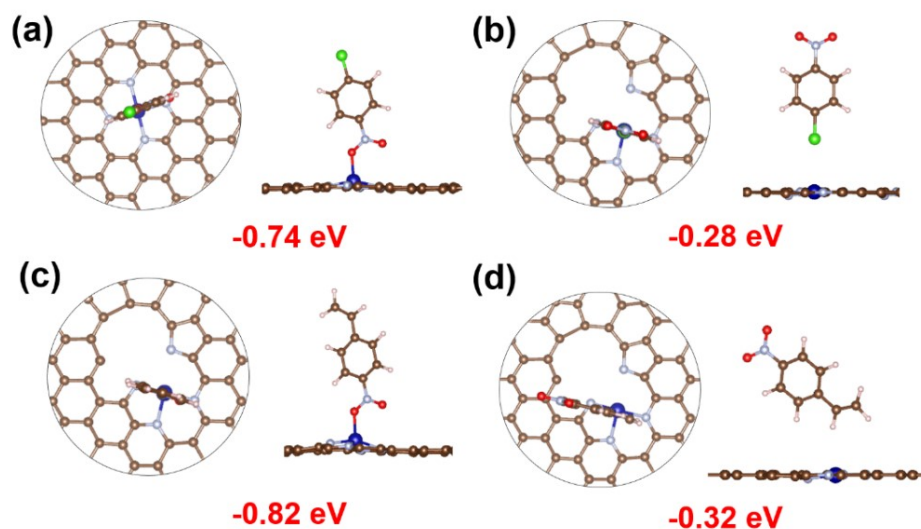
**Fig. S10** (a, e) XPS survey spectra, (b, f) N 1s XPS spectra, (c, g) C 1s XPS spectra, and (d, h) Co 2p XPS spectra of fresh Co-N-CNS-Th and recycled Co-N-CNS-Th after 10 runs.



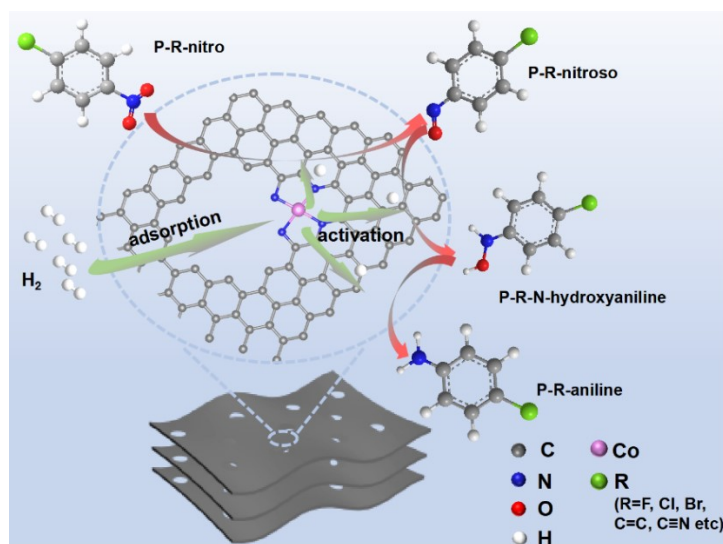
**Fig. S11** (a, d) XPS survey spectra, (b, e) N 1s XPS spectra, and (c, f) Co 2p XPS spectra of collected Co-N-CNS-Th and Co-N-CNS after the H<sub>2</sub>-TPR tests.



**Fig. S12** Adsorption energies of the intermediates in the selective hydrogenation of *p*-CNB process on regular Co-N<sub>4</sub> configuration embedded in graphene and Co-N<sub>4</sub> sites embedded in the micropore defective Co-N-CNS-Th.



**Fig. S13** Optimized structures and adsorption energies of (a) the  $-\text{NO}_2$  and (b)  $-\text{Cl}$  group in  $p$ -CNB. Optimized structures and adsorption energies of (c) the  $-\text{NO}_2$  and (b)  $-\text{CH}=\text{CH}_2$  group in  $p$ -nitrostyrene.



**Fig. S14** Illustration for the reaction path of  $p$ -CNB hydrogenation over Co-N-CNS-Th.



**Table S1.** Physical properties of CNS, Co-N-CNS and Co-N-CNS-Th.

Entry	Catalyst	$I_D/I_G$	Surface area ( $\text{m}^2 \text{g}^{-1}$ )
1	CNS	0.98	198
2	Co-N-CNS	1.12	608
3	Co-N-CNS-Th	1.18	698

**Table S2.** Structural parameters extracted from the Co K-edge EXAFS fitting.

Sample	Path	CN	R( $\text{\AA}$ )	$\sigma^2(\times 10^{-3} \text{\AA}^2)$	$\Delta E_0(\text{eV})$	R factor
Co foil	Co-Co	12	2.49	7	7.4	0.0003
Co-N-CNS-Th	Co-N(O)	4.0	1.87	7	-9.0	0.014
Co-N-CNS	Co-N(O)	4.3	1.87	2.8	-7.1	0.014
	Co-Co	0.4	2.47	1.3		

**Table S3.** The molar and mass composition of Co-N-CNS-Th before and after the cycling test determined by XPS and ICP-OES.

Element	XPS			ICP-OES	
	C/at.%	N/at.%	O/at.%	Co/at.%	Co/wt.%
Before reaction	83.25	10.35	6.21	0.18	0.59
After 10 runs	82.20	11.11	6.48	0.21	0.61

**Table S4.** Catalytic performances of related cobalt-based catalysts for the selective hydrogenation of nitroarenes.

Entry	Catalyst	Reaction conditions	TOF (h <sup>-1</sup> )	
1	Co-N-CNS-Th	2 MPa H <sub>2</sub> , 100 °C	169.8	This work
2	Co-N-CNS	2 MPa H <sub>2</sub> , 100 °C	112.4	This work
3	Co-N-CNS-Th	N <sub>2</sub> H <sub>4</sub> ·H <sub>2</sub> O, 80 °C	345.0	This work
4	Co-N-CNS-Th	NaBH <sub>4</sub> , 30 °C	10188.6	This work
5	Co@NC-1	H <sub>2</sub> , 1 MPa, 30 °C	12.3	Ref. 1
6	Co-N-C	H <sub>2</sub> , 3 MPa, 80 °C	35.9	Ref. 2
7	H-Co-N-C@SiO <sub>2</sub> -20	H <sub>2</sub> , 2.7 MPa, 110 °C	146.0	Ref. 3
8	Co@CN-400	H <sub>2</sub> , 1 MPa, 60 °C	4.8	Ref. 4
9	Co/CoO @Carboon	H <sub>2</sub> , 4 MPa, 120 °C	25.2	Ref. 5
10	Co@mesoNC	H <sub>2</sub> , 3 MPa, 110 °C	42.0	Ref. 6
11	Co@NC-800	N <sub>2</sub> H <sub>4</sub> ·H <sub>2</sub> O, 80 °C	39.8	Ref. 7
12	Fe-Ni NPs	NaBH <sub>4</sub> , 30 °C	17.1	Ref. 8

**Table S5.** Elemental contents of collected Co-N-CNS-Th and collected Co-N-CNS after the H<sub>2</sub>-TPR tests.

<b>Sample</b>	<b>C/at. %</b>	<b>N/at. %</b>	<b>O/at. %</b>	<b>Co/at. %</b>
Fresh Co-N-CNS-Th	69.14	19.50	10.97	0.39
Collected Co-N-CNS-Th	79.08	10.50	10.15	0.26

**Table S6.** Absorption tests of *p*-CNB on CNS, Co-N-CNS, and Co-N-CNS-Th.

<b>Sample</b>	<b>Absorption quantity (<math>\mu\text{mol g}^{-1}</math>)</b>
CNS	11
Co-N-CNS	302
Co-N-CNS-Th	353

## Reference

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