

**Selective hydrogenation of nitroarenes under mild conditions
by the optimization of active sites in a well defined Co@NC
catalyst**

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Text S1

The conversion rate and selectivity were evaluated based on the amount of nitrobenzene. Nitrobenzene conversion rate (mol%), product yield (mol%) and carbon balance:

$$\text{Nitrobenzene conversion} = \left(1 - \frac{\text{Moles of nitrobenzene}}{\text{Moles of nitrobenzene loaded}}\right) \times 100\%$$

$$\text{product yield} = \left(\frac{\text{Moles of product}}{\text{Moles of nitrobenzene loaded}}\right) \times 100\%$$

$$\text{carbon balance} = \left(\frac{\text{Moles of all products}}{\text{Moles of nitrobenzene loaded}}\right) \times 100\%$$

Table S1 TOF of nitrobenzene hydrogenation compare with representative work

No.	Catalyst	Reaction conditions	TOF×10⁻⁴ (s⁻¹)	Refs.
1	Co/CoO @Carbon	H ₂ , 4MPa, 120°C	7.01	[1]
2	Co@CN-400	H ₂ , 1MPa, 60°C	13.3	[2]
3	CeO ₂ nanorods	N ₂ H ₄ ·H ₂ O, 80 °C	13.9	[3]
4	2.5%Co 25%Mo ₂ C/ AC	N ₂ H ₄ ·H ₂ O, 80 °C	4.9	[4]
5	Rh-Fe ₃ O ₄	N ₂ H ₄ ·H ₂ O, 80 °C	9.8	[4]
6	Fe-Ni NPs	NaBH ₄ , rt	47.62	[5]
7	Co@NC-800	N ₂ H ₄ ·H ₂ O, 80 °C	91.1	This study

Table S2 Catalytic Hydrogenation of Nitrobenzene with different pyrolysis temperature

Entry	Catalyst	T (°C)	Time (min)	Yield (%)	Sel (%)
1	Co@NC	600	30	98	83
2	Co@NC	800	30	100	97
3	Co@NC	1000	30	100	70

Table S3 Co weight content in Co@NC, Co-NC and Co@NC (al) by ICP-MS

Catalysts	Co%
Co@NC	36.8
Co-NC	32.1
Co@NC(al)	14.7

Table S4 Atomic ratio of each element in the XPS spectrum

Catalysts	C%	N%	O%	Co%
Co@NC	88.12	4.43	2.45	5
Co-NC	82.88	5.56	3.87	7.69
Co@NC(al)	90.02	9.41	/	0.57

Table S5 Weight ratio of each element in the XPS spectrum

Catalysts	C%	N%	O%	Co%
Co@NC	78.2	4.3	2.7	20.2
Co-NC	62.7	4.9	3.9	28.5
Co@NC(al)	86.8	10.6	/	2.6

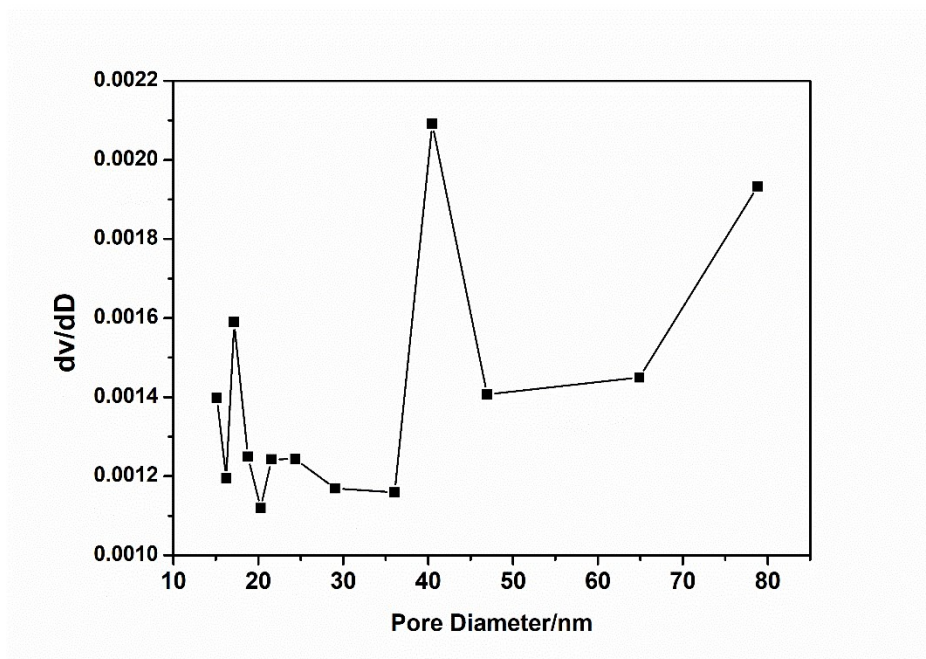


Figure S1 The pore sizes distribution diagram derived of Co@NC

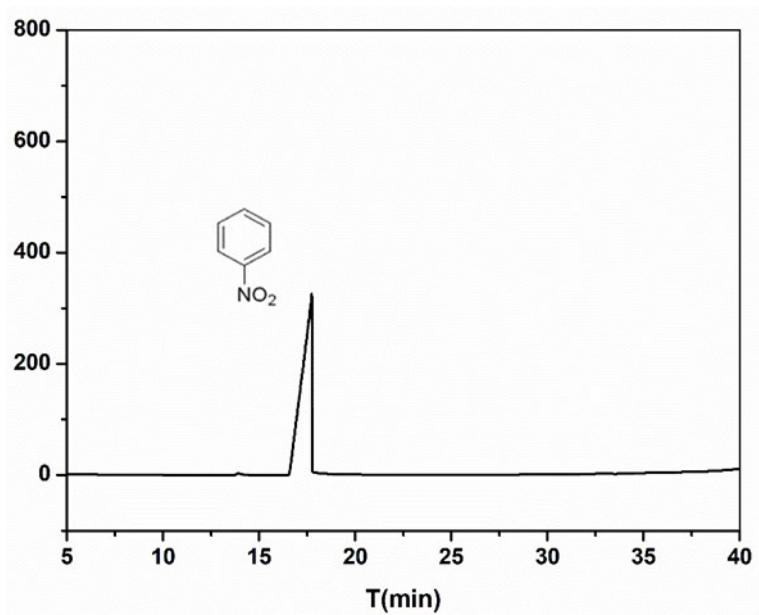


Figure S2 The GC spectra of the solution after reaction. Reaction conditions: 1 mmol of nitrobenzene, 10 mg of catalyst, 5 mL of ethanol

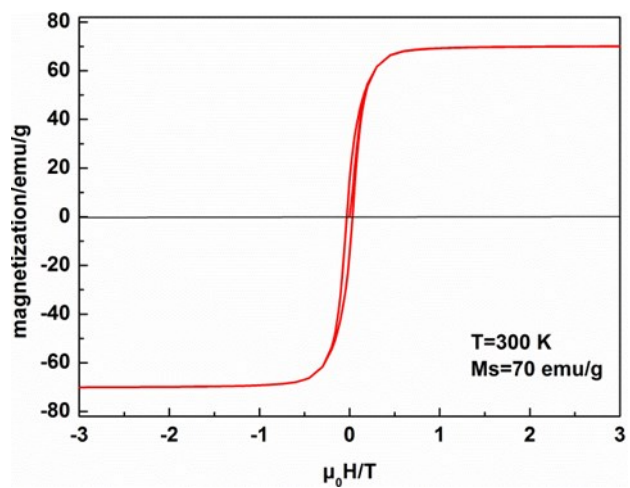


Figure S3 Magnetization data for Co@NC

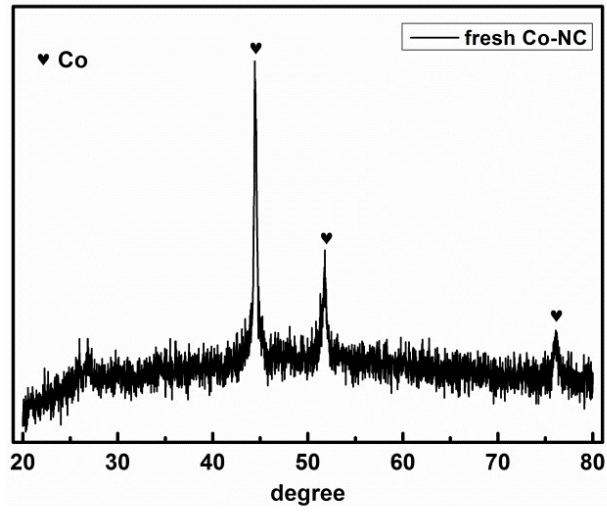


Figure S4 XRD patterns of the Co-NC

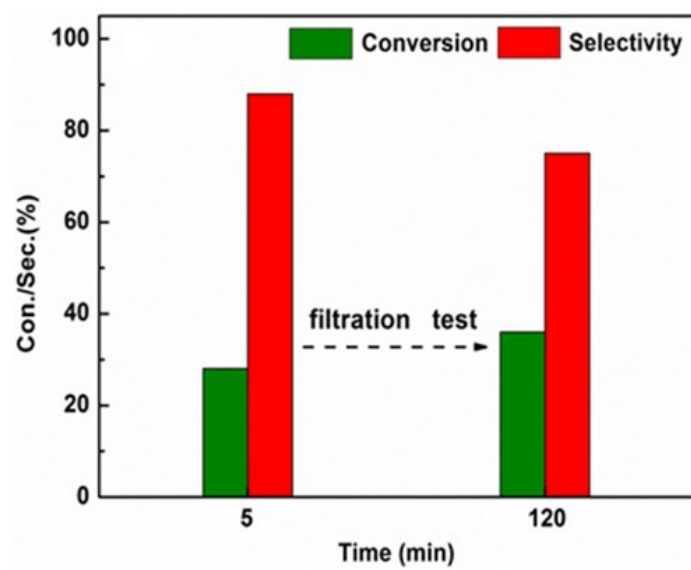


Figure S5 Hot filtration test of the reduction of nitrobenzene with Co@NC as a catalyst.

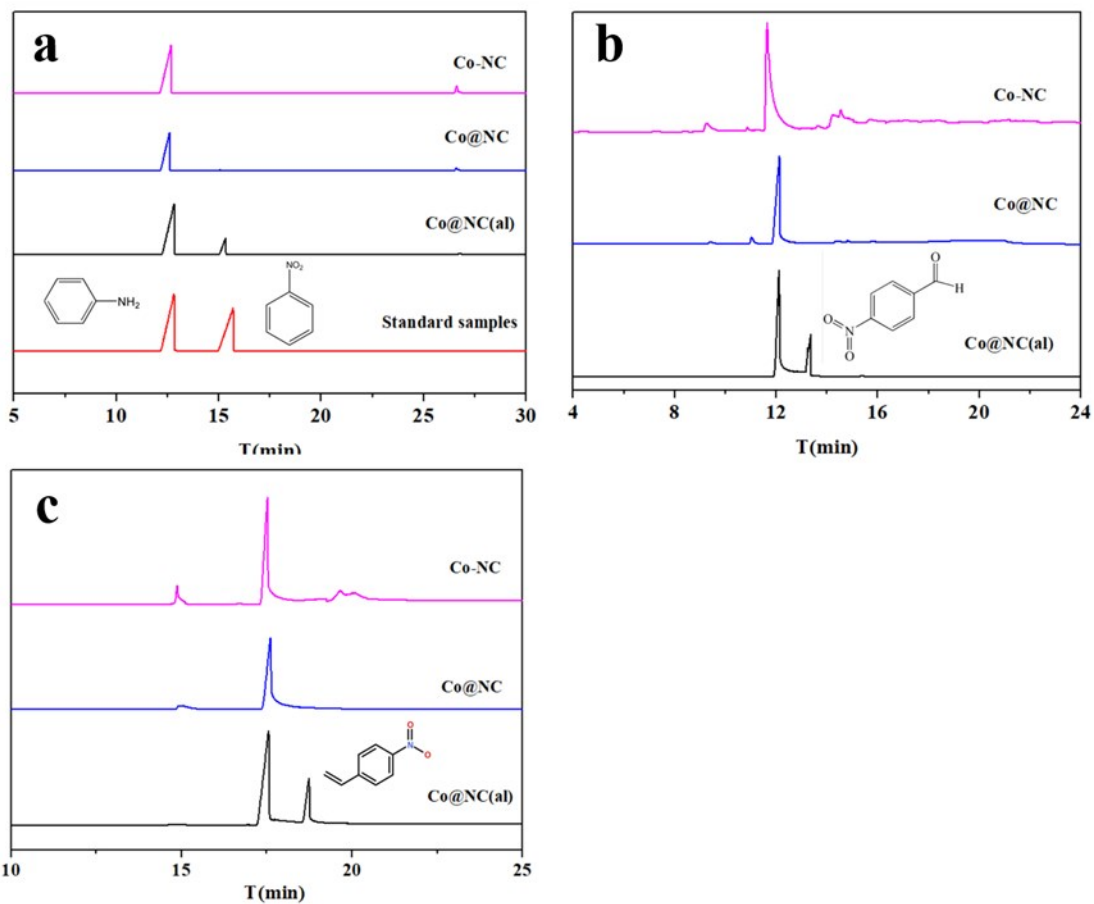


Figure S6. The GC spectra of the solution after reaction. (a) Nitrobenzene hydrogenation (b) p-nitrobenzaldehyde hydrogenation (c) p-nitrostyrene hydrogenation
Reaction conditions: 1 mmol of nitrobenzene, 10 mg of catalyst, 5 mL of ethanol

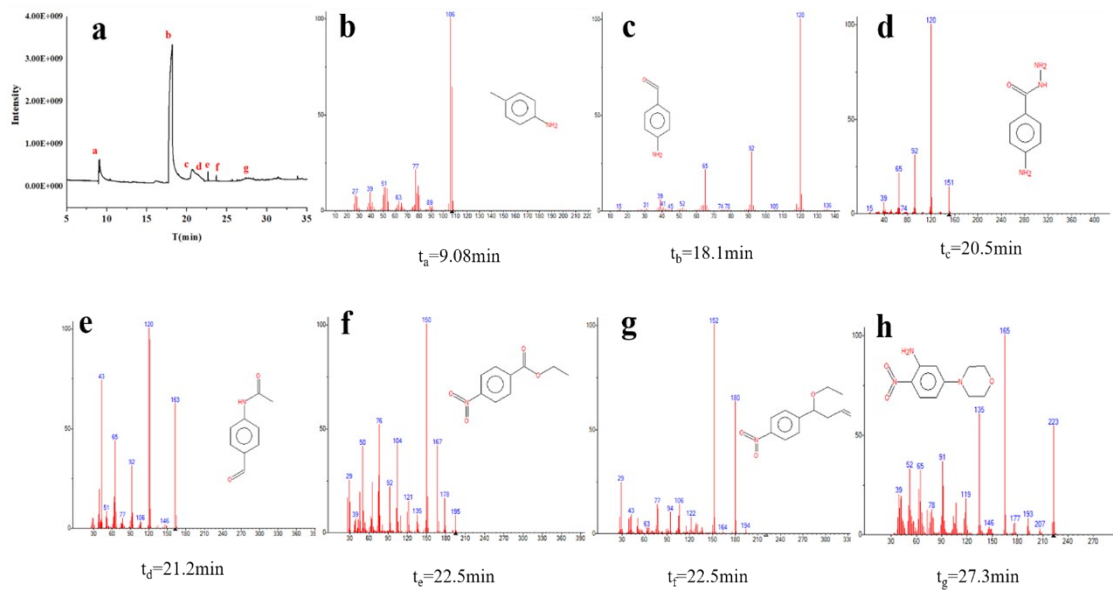


Figure S7. GC-MS analysis of Co-NC catalyst for p-nitrobenzaldehyde hydrogenation

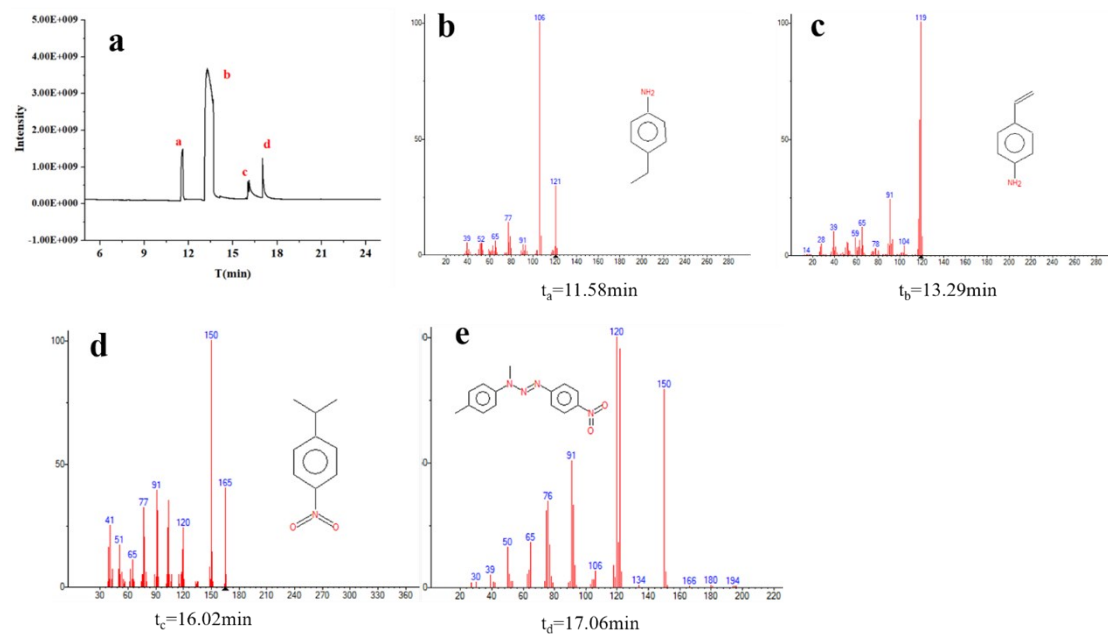


Figure S8. GC-MS analysis of Co-NC catalyst for p-nitrostyrene hydrogenation

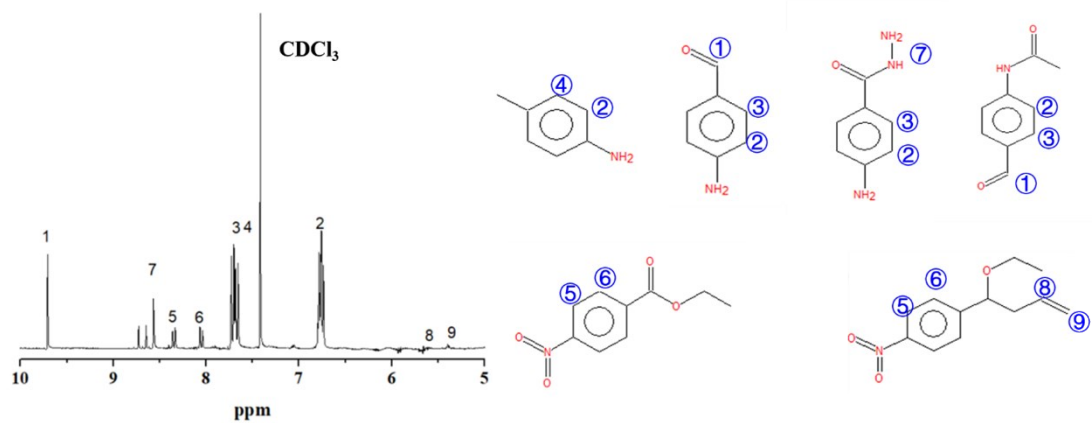


Figure S9. ^1H NMR spectra analysis of Co-NC catalyst for p-nitrobenzaldehyde hydrogenation

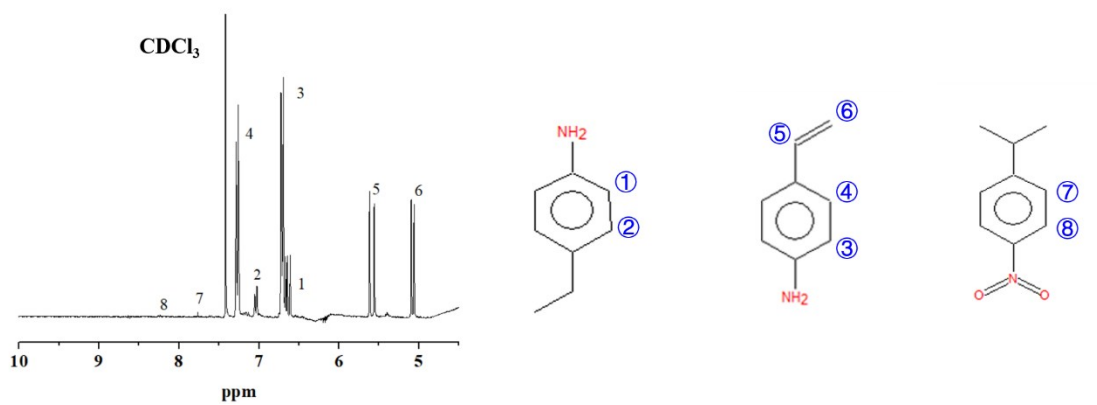


Figure S10. ^1H NMR spectra analysis of Co-NC catalyst for p-nitrostyrene hydrogenation

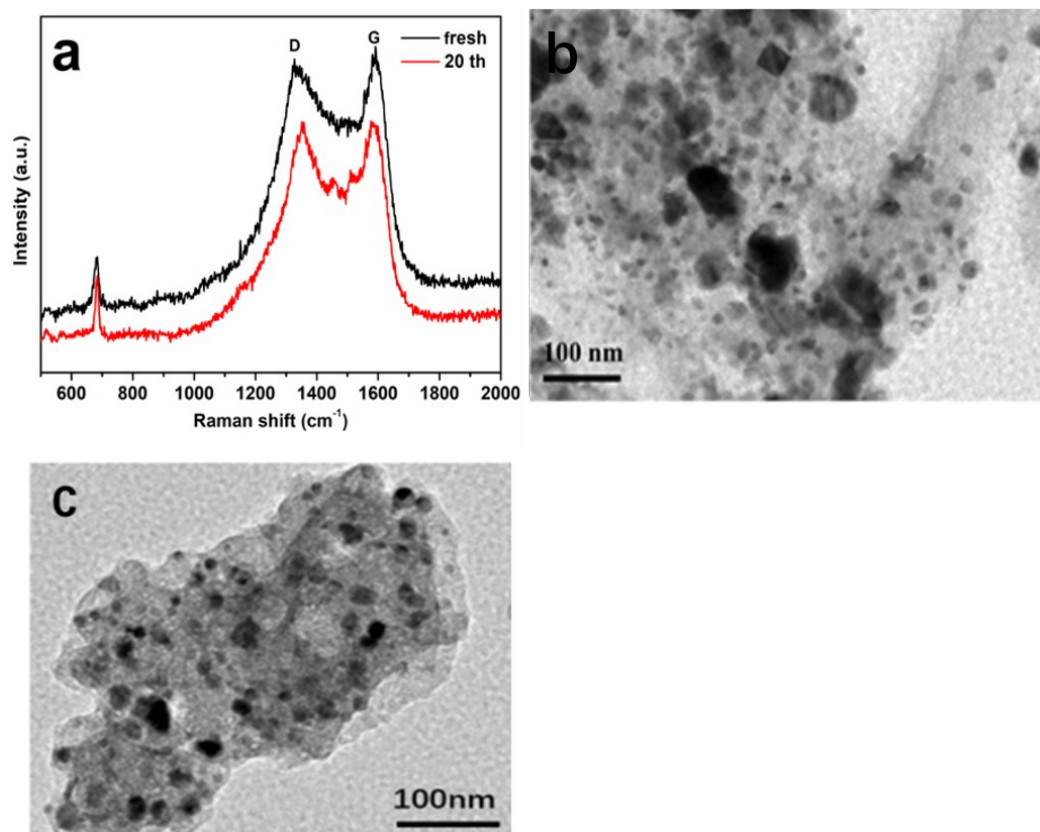


Figure S11 (a) Raman shift of Co@NC and after 20th-Co@NC, (b,c) Representative TEM image of Co-NC and Co@NC

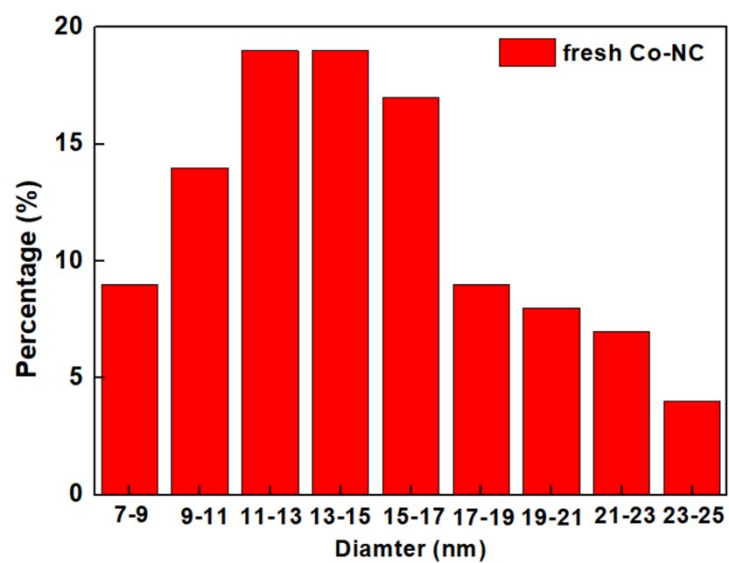


Figure S12 The metal particle size distribution histogram of fresh Co-NC

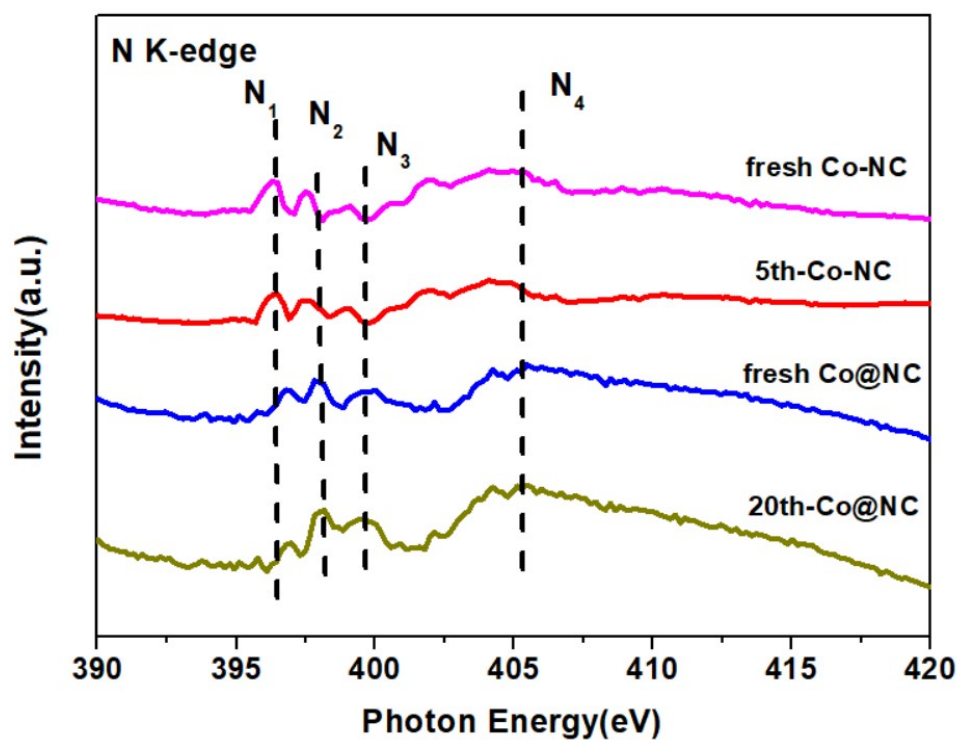


Figure S13 XANES N K-edge spectra of fresh Co-NC, 5th-Co-NC, fresh Co@NC and 20th-Co@NC respectively

References

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