Supporting Information

Enhanced catalytic reduction of nitroaromatics by atomically dispersed cobalt catalyst via sulfur doping

Jinna Lu,†[a] Qiong Wu,†[b] Bolin Li,[a] Ye Li,[a] Kaixiong Yang*[c] and Li Ye*[a]

[a] Hubei Key Laboratory of Mineral Resources Processing and Environment, School of Resources and Environmental Engineering, Wuhan University of Technology, Wuhan 430070, China

[b] Technical Centre for Soil, Agriculture and Rural Ecology and Environment, Ministry of Ecology and Environment, Beijing 100012, China

[c] China Construction Advanced Technology Research Institute, China Construction Third Engineering Bureau Group Co., Ltd., Wuhan 430075, China

* Corresponding author: Kaixiong Yang, Li Ye

E-mail: yang_kaixiong@126.com, yeli1992@whut.edu.cn

† Co-first authorship

Number of pages: 10

Number of figures: 5

Number of tables: 2

Table of Contents

Figs:

Tables:

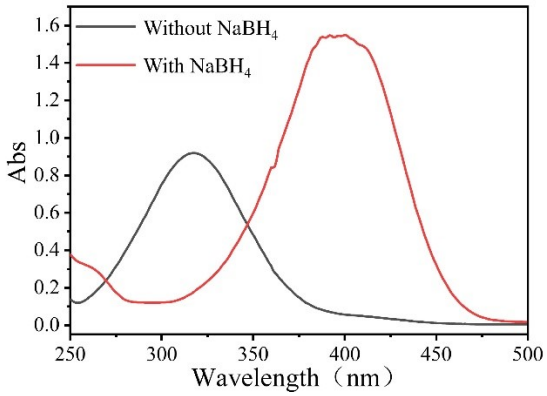

Fig. S1 Time-dependent UV-vis spectra recorded with and without the addition of $NaBH_4$ into 4-NP solution.

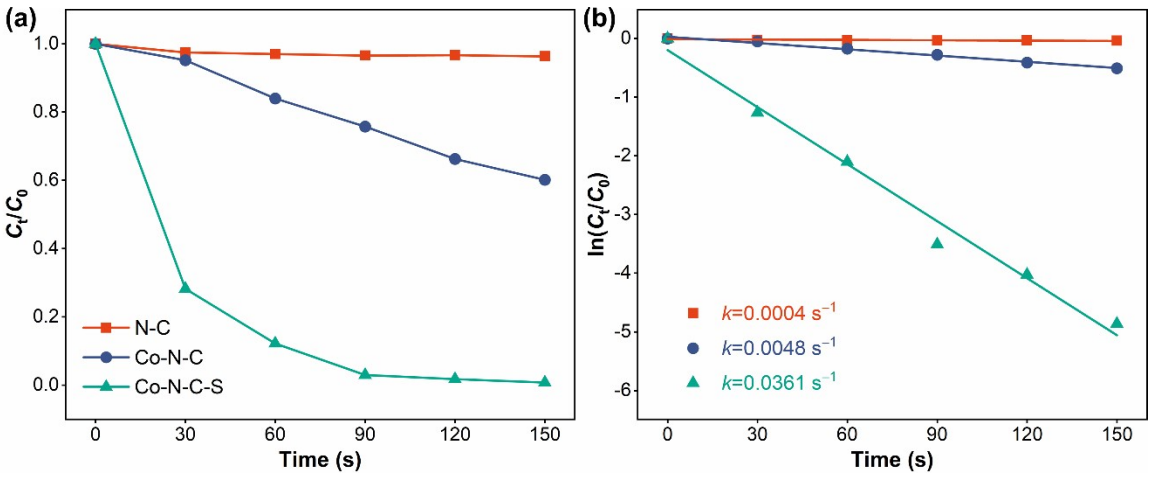

Fig. S2 Catalytic performance (a) and *k* values (b) of the N-C, Co-N-C, and Co-N-C-S. Reaction conditions: [4-NP] = 0.15 mM, [catalyst loading] = 50 mg·L^{-1}, and [$NaBH_4$] = 30 mM.

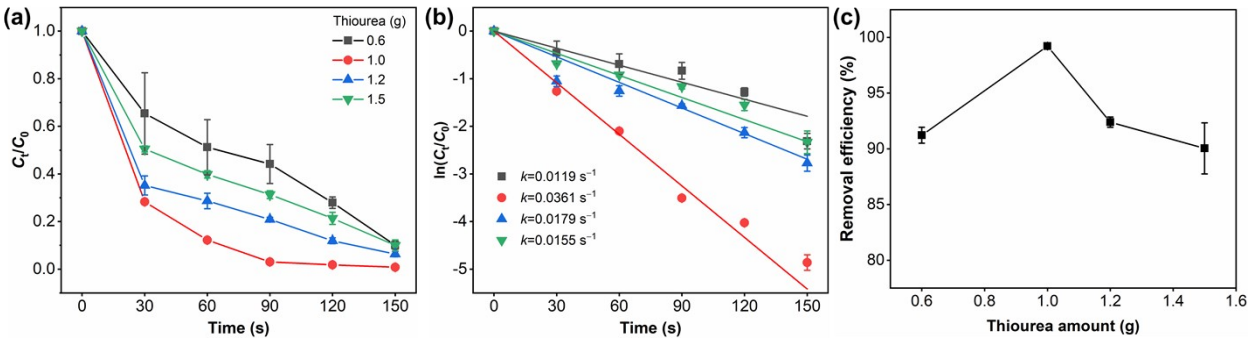

Fig. S3 Catalytic performance of Co-N-C-S catalysts prepared with different thiourea amounts.

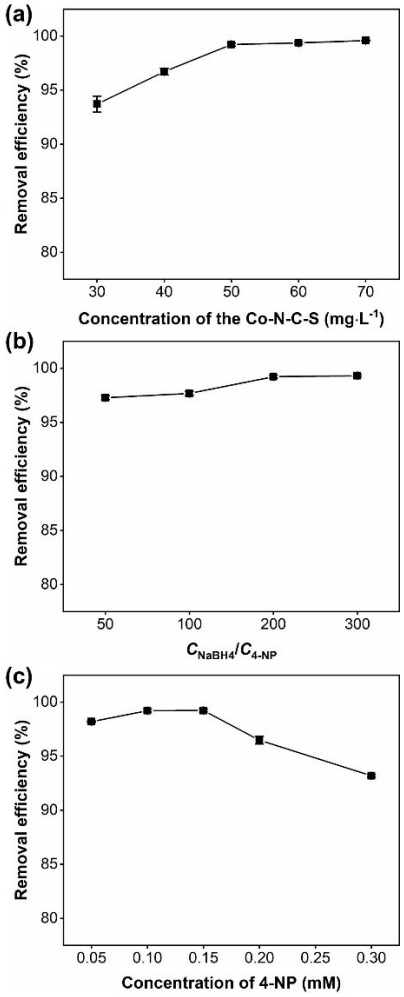

Fig. S4 Effects of the catalyst loading (a), $NaBH_4$ concentration (b), and initial 4-NP concentration (c) on the removal efficiency of 4-NP. Reaction conditions: [4-NP] = 0.15 mM and [$NaBH_4$] = 30 mM (a); [4-NP] = 0.15 mM and [catalyst loading] = 50 mg·L^{-1} (b); [catalyst loading] = 50 mg·L^{-1} and [$NaBH_4$] = 30 mM (c).

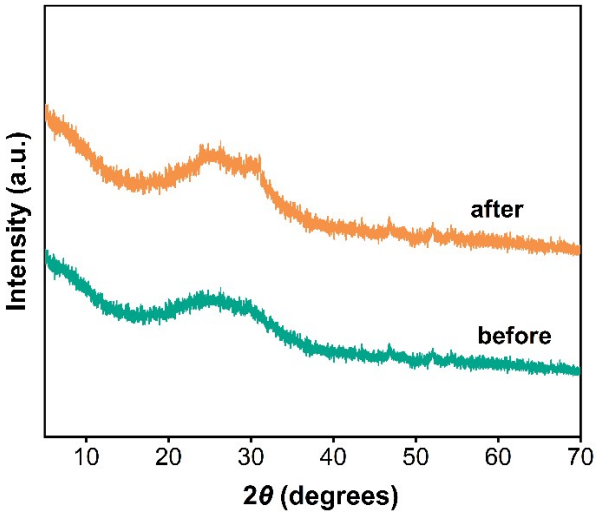

Fig. S5 XRD patterns of Co-N-C-S before and after six catalytic cycles.

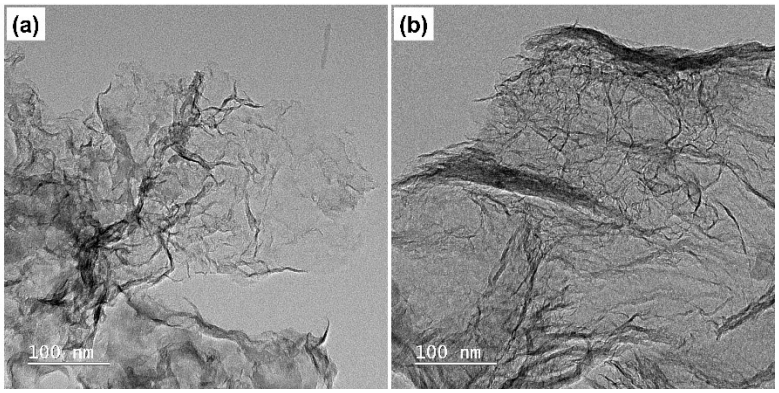

Fig. S6 TEM images of Co-N-C-S before (a) and after (b) six catalytic cycles.

Table S1 The fraction of pyridinic N and pyrrolic N in N-C, Co-N-C, and Co-N-C-S.

Samples	States	Fractions (%)
N-C	Pyridinic N	16.89
	Pyrrolic N	83.11
Co-N-C	Pyridinic N	38.06
	Pyrrolic N	61.94
Co-N-C-S	Pyridinic N	46.38
	Pyrrolic N	53.62

Table S2 Catalytic activities of 4-NP reduction on different metal catalysts.

Catalysts	Reduction time (s)	k (s^{-1})	nNaBH4/n4-NP	Reference
Au/graphene hydrogel	720	0.00317	1000	1
$Au/CeO_2@ZrO_2$	1300	0.0241	12.3	2
$Au@g\text{-}C_3N_4$	600	0.0150	10	3
Ni@Pd/KCC-1	290	0.0204	833.3	4
Pt-Au-PDA/RGO	180	0.00958	111.1	5
Au/CB	360	0.0138	100, 200, 300, 400	6
Ag_x/C15h	20	0.0125	500	7
$PDA\text{-}g\text{-}C_3N_4$/Au	60	0.0216	50, 100, 200, 300, 400	8
Fe_3O_4@COF-Au	1440	0.00370	440	9
Co-N-C-S	**150**	**0.0361**	**200**	**This work**

Table S3 The summary of all experimental conditions.

Experiments	Reaction conditions		
	[4-NP] (mM)	[catalyst loading] ($mg \cdot L^{-1}$)	[$NaBH_4$] (mM)
Comparison of performance among three materials	0.15	50	30
Effects of the catalyst loading on the performance of the Co-N-C-S	0.15	30, 40, 50, 60, 70	30
Effects of the $NaBH_4$ concentration on the performance of the Co-N-C-S	0.15	50	7.5, 15, 30, 45
Effects of the initial 4-NP concentration on the performance of the Co-N-C-S	0.05, 0.10, 0.15, 0.20, 0.30	50	30
Cyclic experiments	0.15	50	30
Catalytic performance of the Co-N-C-S in different water matrices	0.15	50	30

References:

1. J. Li, C.-y. Liu and Y. Liu, Au/graphene hydrogel: synthesis, characterization and its use for catalytic reduction of 4-nitrophenol, *J. Mater. Chem.*, 2012, **22**, 8426-8430.
2. V. Evangelista, B. Acosta, and S. Miridonov*, et al.*, Highly active Au-CeO_2@ZrO_2 yolk–shell nanoreactors for the reduction of 4-nitrophenol to 4-aminophenol, *Appl. Catal. B*, 2015, **166-167**, 518-528.
3. T. B. Nguyen, C. P. Huang and R.-a. Doong, Enhanced catalytic reduction of nitrophenols by sodium borohydride over highly recyclable Au@graphitic carbon nitride nanocomposites, *Appl. Catal. B*, 2019, **240**, 337-347.
4. Z. Dong, X. Le, and C. Dong*, et al.*, Ni@Pd core–shell nanoparticles modified fibrous silica nanospheres as highly efficient and recoverable catalyst for reduction of 4-nitrophenol and hydrodechlorination of 4-chlorophenol, *Appl. Catal. B*, 2015, **162**, 372-380.
5. W. Ye, J. Yu, and Y. Zhou*, et al.*, Green synthesis of Pt–Au dendrimer-like nanoparticles supported on polydopamine-functionalized graphene and their high performance toward 4- nitrophenol reduction, *Appl. Catal. B*, 2016, **181**, 371-378.
6. L. Qin, H. Yi, and G. Zeng*, et al.*, Hierarchical porous carbon material restricted Au catalyst for highly catalytic reduction of nitroaromatics, *J. Hazard. Mater.*, 2019, **380**, 120864.
7. C.-S. Chen, T.-C. Chen, and K.-L. Chiu*, et al.*, Silver particles deposited onto magnetic carbon nanofibers as highly active catalysts for 4-nitrophenol reduction, *Appl. Catal. B*, 2022, **315**, 121596.
8. L. Qin, D. Huang, and P. Xu*, et al.*, In-situ deposition of gold nanoparticles onto polydopamine-decorated g-C_3N_4 for highly efficient reduction of nitroaromatics in environmental water purification, *J. Colloid Interface Sci.*, 2019, **534**, 357-369.
9. Y. Xu, X. Shi, and R. Hua*, et al.*, Remarkably catalytic activity in reduction of 4-nitrophenol and methylene blue by Fe_3O_4@COF supported noble metal nanoparticles, *Appl. Catal. B*, 2020, **260**, 118142.