Electronic Supplementary Information (ESI)

The main factor to improve the performance of $CoSe_2$ for photocatalytic CO_2 reduction: element doping or phase transformation

Yong Xu,[ab] Jiang Mo,[a] Guanqun Xie,[a] Xiaoxia Wang,*[a] and Shujiang Ding*[b]

[a]*School of Materials Science and Engineering, Dongguan University of Technology, Dongguan 523808, China.*

[b]*Department of Applied Chemistry, School of Science, Xi´an Jiaotong University, Xi´an, 710049, P.R. China*

*Corresponding Author
E-mail: wangxx@dgut.edu.cn; dingsj@mail.xjtu.edu.cn

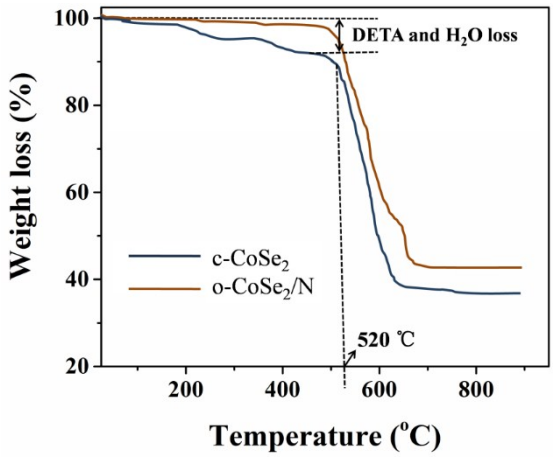

Fig. S1. TGA curves of c-$CoSe_2$ and o-$CoSe_2$/N. The experimental conditions are as follows: the heating rate of 10 °C/min under N_2 flow.

The TGA curve of c-$CoSe_2$ shows distinct three steps of weight loss. 4.6 wt% of c-$CoSe_2$ was lost from room temperature to 280 °C, which was mainly due to the evaporation of adsorbed water and free DETA. The second stage of weight loss was brought about by the decomposition of DETA intercalated in the nanosheet structure, where 4.4 wt% weight was lost between 330 °C and 480 °C. After that, the weight of c-$CoSe_2$ began to drop rapidly because of the thermal decomposition of the sample. However, the weight of o-$CoSe_2$/N declined slowly before 500 °C and it may be caused by the removal of water and DETA in o-$CoSe_2$/N during the process of phase change.

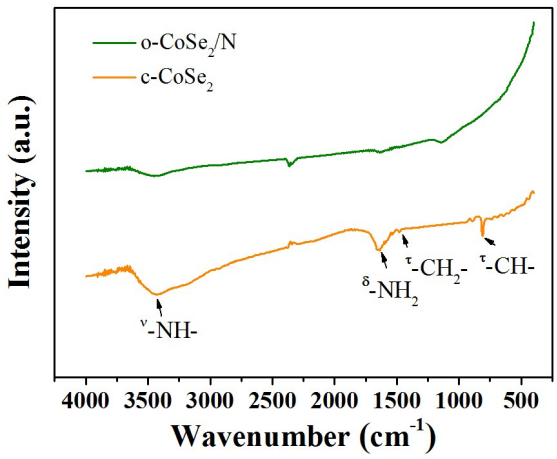

Fig. S2. FTIR spectra of of c-$CoSe_2$ and o-$CoSe_2$/N.

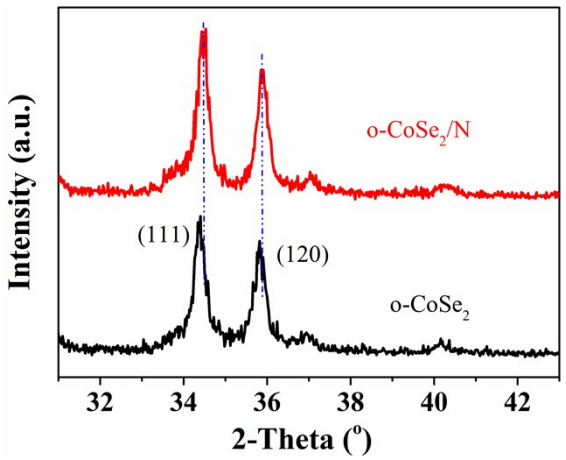

Fig. S3. The comparison of (111) and (120) diffraction peaks between o-$CoSe_2$/N and pristine o-$CoSe_2$ in selected XRD patterns.

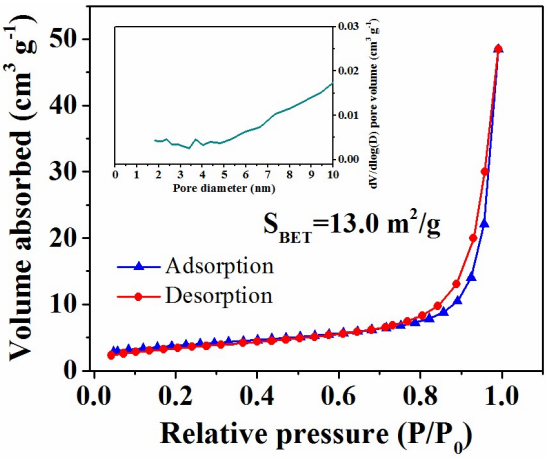

Fig. S4. N_2 adsorption-desorption isotherms of c-$CoSe_2$ along with corresponding pore size distribution.

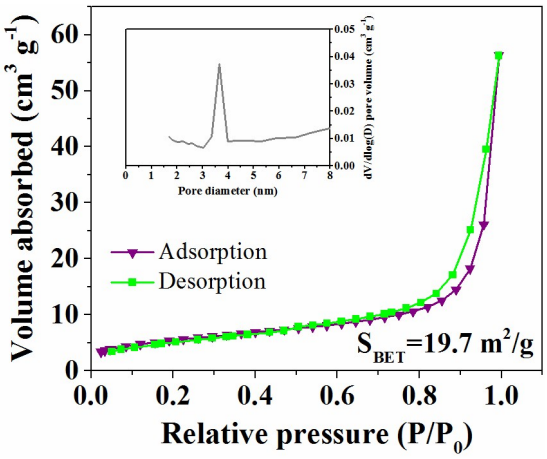

Fig. S5. N_2 adsorption-desorption isotherms of o-$CoSe_2$/N along with corresponding pore size distribution.

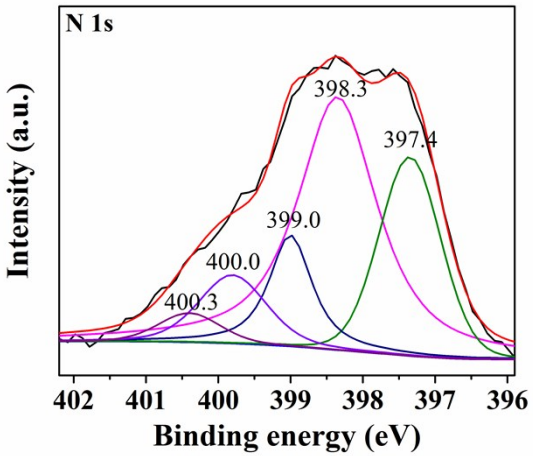

Fig. S6. High resolution XPS of N 1s for o-$CoSe_2$/N.

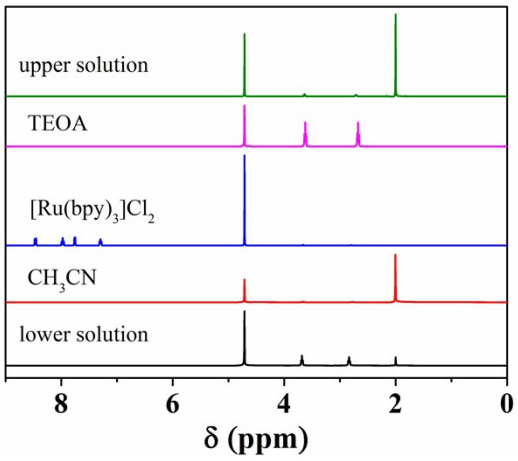

Fig. S7. ^{1}H NMR spectra of TEOA, photosensitizer, CH_3CN and liquid phase substances after photoreaction.

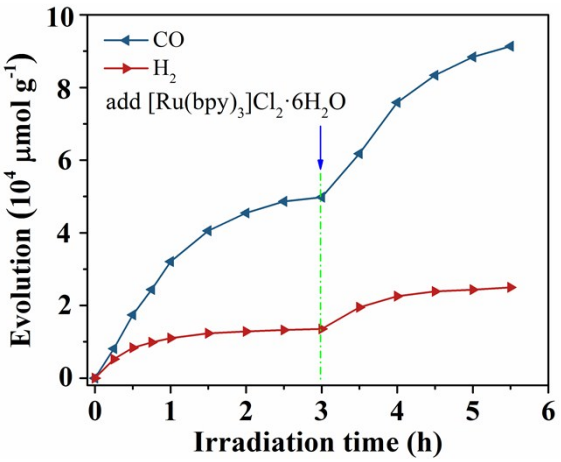

Fig. S8. The curves of catalytic activity by adding photosensitizer after 3 h of illumination.

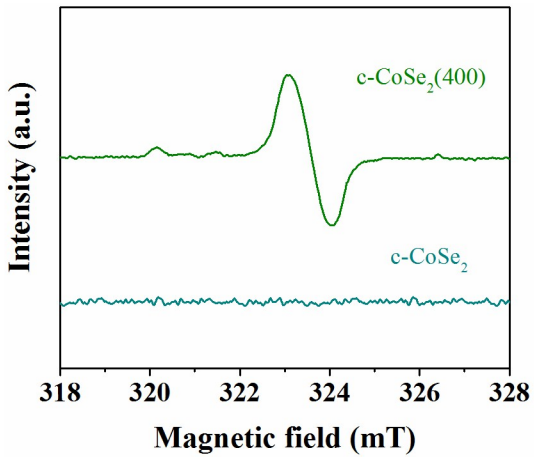

Fig. S9. ESR spectra of c-$CoSe_2$ and c-$CoSe_2$(400). The c-$CoSe_2$(400) shows an obvious ESR signal with *g* value of 2.0015, indicating the existence of Se vacancies.

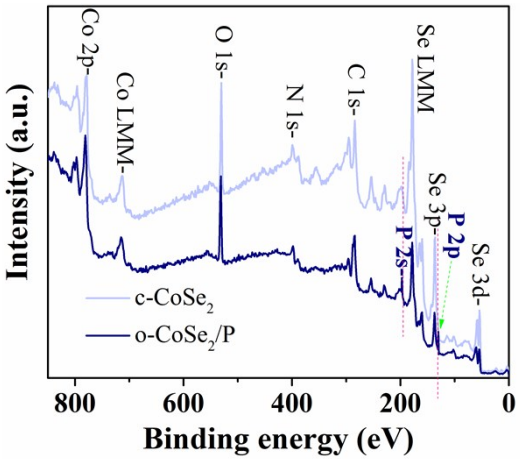

Fig. S10. XPS survey spectra of c-$CoSe_2$ and o-$CoSe_2$/P.

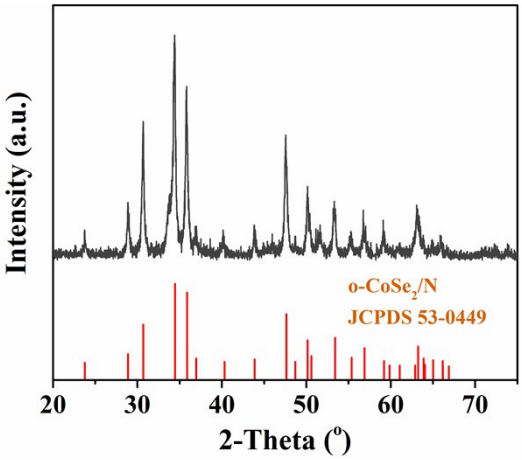

Fig. S11. XRD pattern of o-$CoSe_2$/N after four recycles.

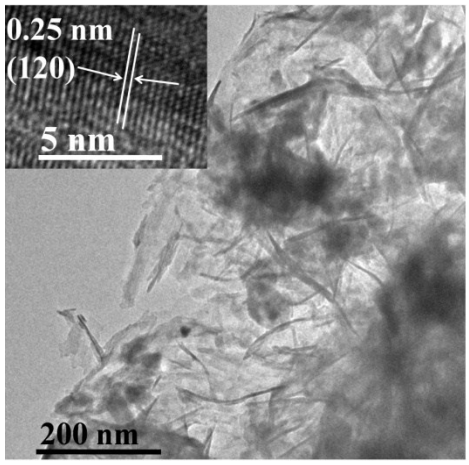

Fig. S12. TEM image of o-$CoSe_2$/N after four recycles.

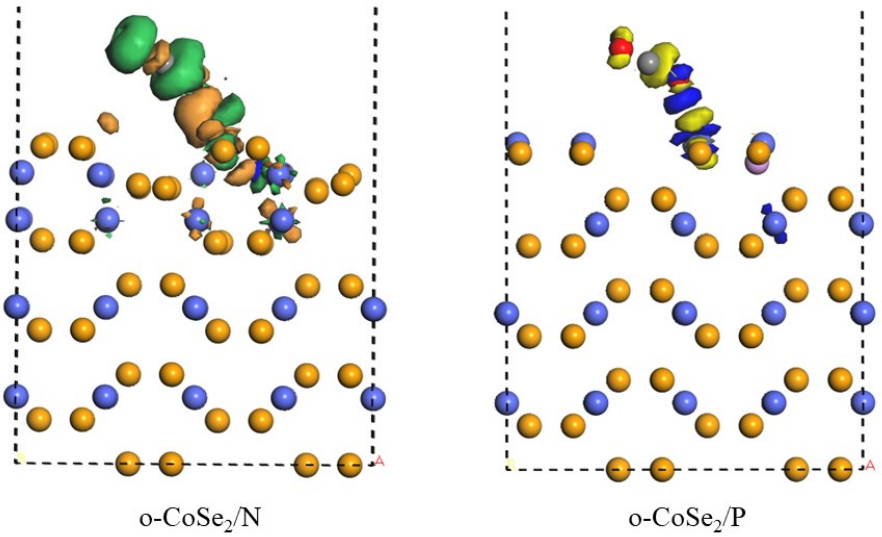

Fig. S13. Charge difference of CO_2 adsorbed on o-$CoSe_2$/N and o-$CoSe_2$/P.

Table S1. Control experiments of photocatalytic CO_2 reduction.

Entry	Catalyst/ o-$CoSe_2$/N	Photosensitizer/ $[Ru(bpy)_3]Cl_2$	CO_2	TEOA	Light	Yield of CO (μmol)	Yield of H_2 (μmol)
1	×	√	√	√	√	0	1.6
2	√	×	√	√	√	0	0
3[a]	√	√	×	√	√	0	14.4
4	√	√	√	×	√	0	0
5	√	√	√	√	×	0	0.1
6	√	√	√	√	√	49.8	13.5

Conditions: o-$CoSe_2$/N (1 mg), $[Ru(bpy)_3]Cl_2$ (5 mg), acetonitrile/H_2O/TEOA = 4 mL : 1 mL : 1.5 mL in the quartz tube of 55 mL, CO_2 (1 atm), irradiation with white LEDs lamp at room temperature. [a]Degassed with argon.

Table S2. The comparisons of photocatalytic CO_2 reduction performance of o-$CoSe_2$ and other Co-based catalyst.

Entry	Catalyst	average rate of CO (μmol h^{-1} g^{-1})			Reference
		1h	2h	3h	
1	o-$CoSe_2$/N	32,000		16,600	This work
2	o-$CoSe_2$/P			10,476	This work
3	o-$CoSe_2$ (pure phase)			8,806	This work
4	c-$CoSe_2$	13,668		8,402	This work
5	Co-Co_2P@NPC	63,000		35,000	Our previous work [1]
6	$Co_{1.11}Te_2$⊂C	23,000		11,400	Our previous work [2]
7	Zn/Co-C-BMZIF (3:1)			11,000	Ref. [4]
8	$CoSn(OH)_6$	18,700			[3]
9	Co_3O_4-NS	9,040 μmol h^{-1} g^{-1} in 6 h			[4]
10	Co_3O_4	3,523		2,003	Ref. [12]
11	PMMCoCC-1200	187 μmol h^{-1} g^{-1} in 6 h			[5]
12	$ZnCo_2O_4$			45	Ref. [9]
13	$CuCo_2O_4$	22.9			[6]
14	Co-POM	17 μmol h^{-1} g^{-1} in 7 h			[7]
15	Co_6-MOF			13.1	[8]

[1] Y. Xu, J. Mo, Z. Fu, S. Liu, Z. Yang and W. Fu, *Chem. Eur. J.*, 2018, **24**, 8596–8602.

[2] Y. Xu, J. Mo, G. Xie, D. Ding, S. Ding, X. Wang and C. Li, *Chem. Commun.*, 2019, **55**, 6862–6865.

[3] X. Lin, Y. Gao, M. Jiang, Y. Zhang, Y. Hou, W. Dai, S. Wang and Z. Ding, *Appl. Catal. B: Environ.*, 2018, **224**, 1009–1016.

[4] W. Chen, B. Han, C. Tian, X. Liu, S. Liang, H. Deng and Z. Lin, *Appl. Catal. B: Environ.*, 2019, **244**, 996–1003.

[5] K. Zhao, S. Zhao, C. Gao, J. Qi, H. Yin, D. Wei, M. F. Mideksa, X. Wang, Y. Gao, Z. Tang and R. Yu, *Small*, 2018, **14**, 1800762.

[6] M. Jiang, Y. Gao, Z. Wang and Z. Ding, *Appl. Catal. B: Environ.*, 2016, **198**, 180–188.

[7] G. Zhao, H. Pang, G. Liu, P. Li, H. Liu, H. Zhang, L. Shi and J. Ye, *Appl. Catal. B: Environ.*, 2017, **200**, 141–149.

[8] J. Zhao, Q. Wang, C. Sun, T. Zheng, L. Yan, M. Li, K. Shao, X. Wang and Z. Su, *J. Mater. Chem. A*, 2017, **5**, 12498–12505.