Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

One-step synthesis of ZnS-N/C nanocomposites derived from Zn-based chiral metal-organic frameworks with high photocatalytic activity for selective oxidation of *cis*-cyclooctene

Supporting Information

Xiaoling Lin,[a] Beibei Liu,[a] Hui Huang,[a] Chunfeng Shi,[b]* Yang Liu[a]* and Zhenhui Kang[a]**

[a] Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Institute of Functional Nano & Soft Materials (FUNSOM), Soochow University, 199 Ren'ai Road, Suzhou, 215123, China

E-mail: hhuang0618@suda.edu.cn, yangl@suda.edu.cn, zhkang@suda.edu.cn

[b] State Key Laboratory of Catalytic Materials and Reaction Engineering, Research Institute of Petroleum Processing, SINOPEC, Beijing 100083, China

E-mail: shicf.ripp@sinopec.com

Table S1. Crystal data and structure refinements for compounds **L-1** and **D-1**.

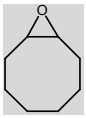
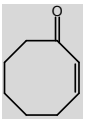
	L-1	**D-1**
Empirical formula	$C_{20}H_{17}Cl_2N_3O_4SZn$	$C_{20}H_{17}Cl_2N_3O_4SZn$
Formula weight	531.70	531.70
Crystal system	Monoclinic	Monoclinic
Space group	*C*2	*C*2
a (Å)	17.3215(10)	17.3808(10)
b (Å)	10.3684(6)	10.3874(6)
c (Å)	14.0444(8)	14.2015(13)
α (deg)	90.00	90.00
β (deg)	124.8310(10)	125.0040(10)
γ (deg)	90.00	90.00
V (Å^3)	2070.4(2)	2100.2(3)
Z	4	4
D_c (g/cm^3)	1.706	1.682
μ (mm^{-1})	1.580	1.557
F (000)	1080.0	1080.0
Collcd reflns	5520	5503
Unique reflns	3562	3084
parameters	280	280
R_{int}	0.0224	0.0153
GOF	0.884	0.989
R_1[a] [I>2σ (I)]	0.0238	0.0189
wR_2[b] (all data)	0.0489	0.0461

Table S2. Selected bond lengths (Å) and angles (°) for **L-1** and **D-1**

L-1			
Zn(1)-O(2)#1	1.9664(19)	Zn(1)-N(2)	2.058(2)
Zn(1)-N(1)	1.952(2)	Zn(1)-N(3)#2	2.077(2)
O(2)#1-Zn(1)-N(2)	102.31(9)	N(1)-Zn(1)-N(2)	118.71(9)
O(2)#1-Zn(1)-N(3)#2	96.06(9)	N(1)-Zn(1)-N(3)#2	111.71(9)
N(1)-Zn(1)-O(2)#1	121.62(10)	N(2)-Zn(1)-N(3)#2	102.73(9)
D-1			
Zn(1)-O(2)#1	1.9601(16)	Zn(1)-N(2)	2.0662(19)
Zn(1)-N(1)	1.9452(19)	Zn(1)-N(3)#2	2.0766(18)
O(2)#1-Zn(1)-N(2)	101.98(8)	N(1)-Zn(1)-N(2)	118.59(8)
O(2)#1-Zn(1)-N(3)#2	96.41(7)	N(1)-Zn(1)-N(3)#2	111.61(8)
N(1)-Zn(1)-O(2)#1	121.71(8)	N(2)-Zn(1)-N(3)#2	102.97(8)

Symmetry code: (#1) 1/2-x,1/2+y,-z, (#2) 1-x,1+y,1-z for **L-1** (#1) 1/2-x,-1/2+y,-z, (#2) 1-x,-1+y,1-z for **D-1**.

Table S3. The effect of reaction time on selective oxidation of *cis*-cyclooctene with error under visible light irradiation.[a]

Reaction time (h)	Product Selectivity (%)		Conversion (%)	$\Sigma_{sel}C_8$[b]
				
0	0	0	0	0
8	78.32(1.4)	13.47(1.3)	19.31(1.2)	99.98(1.0)
16	81.56(1.3)	10.44(1.3)	28.18(1.3)	99.79(1.1)
24	84.25(1.3)	9.49(1.2)	36.02(1.1)	99.72(1.0)
32	86.75(1.1)	7.54(1.3)	46.56(1.2)	99.51(1.2)
40	90.52(1.0)	5.21(1.3)	57.58(1.0)	99.35(1.2)
48	93.42(0.5)	3.96(1.4)	66.32(0.5)	99.29(1.2)

[a]Reaction conditions: Zn-N/C nanocomposites (0.05 g), *cis*-cyclooctene (10 mL), TBHP (0.5 mL), 80°C, under visible light irradiation. [b]Total selectivity to C_8 partial oxidation products.

Table S4. The conversion of *cis*-cyclooctene and selectivity for epoxycyclooctane with error on the reaction time under visible light irradiation by using different catalysts. [a]

Reaction time (h)	ZnS-N/C		N-doped carbon		ZnS		ZnS/C		none	
	Conversion (%)	Product selectivity (%)	Conversion (%)	Product selectivity (%)	Conversion (%)	Product selectivity (%)	Conversion (%)	Product selectivity (%)	Conversion (%)	Product selectivity (%)
0	0	0	0	0	0	0	0	0	0	0
8	19.31 (1.2)	78.32 (1.4)	1.23 (1.4)	13.67 (1.4)	2.35 (1.4)	3.63 (1.5)	10.32 (1.4	43.32 (1.3)	0.13 (0.1)	0.27 (0.1)
16	28.18 (1.3)	81.56 (1.3)	3.75 (1.4)	14.95 (1.3)	5.65 (1.4)	3.98 (1.4)	13.46 (1.3)	54.55 (1.3)	0.15 (0.1)	0.29 (0.1)
24	36.02 (1.1)	84.25 (1.3)	7.89 (1.3)	11.73 (1.3)	9.27 (1.3)	4.23 (1.4)	17.58 (1.2)	51.53 (1.3)	0.18 (0.1)	0.23 (0.1)
32	46.56 (1.2)	86.75 (1.1)	11.37 (1.2)	10.26 (1.2)	10.75 (1.3)	5.21 (1.4)	21.33 (1.1)	60.28 (1.3)	0.17 (0.1)	0.29 (0.1)
40	57.58 (1.0)	90.52 (1.0)	13.53 (1.1)	8.76 (1.2)	12.23 (1.3)	5.86 (1.4)	23.56 (1.1)	58.79 (1.2)	0.15 (0.1)	0.27 (0.1)
48	66.32 (0.5)	93.42 (0.5)	15.74 (1.1)	4.32 (1.4)	13.02 (1.2)	5.32 (1.3)	25.47 (1.0)	59.92 (1.2)	0.19 (0.1)	0.23 (0.1)

[a]Reaction conditions: 0.05 g catalysts (ZnS-N/C nanocomposites, N-doped carbon, ZnS ZnS/C nanocomposites and without catalyst), *cis*-cyclooctene (10 mL), TBHP

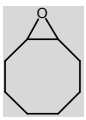
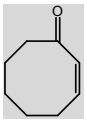
(0.5 mL), 80°C, under visible light irradiation.

Table S5. The conversion of *cis*-cyclooctene and selectivity for epoxycyclooctane with error on reaction time under visible light irradiation by using ZnS-N/C nanocomposites with different atmosphere.[a]

Reaction time (h)	O_2		N_2	
	Conversion (%)	Product selectivity (%)	Conversion (%)	Product selectivity (%)
0	0	0	0	0
8	19.31(1.2)	78.32(1.4)	0.76(1.5)	2.33(1.5)
16	28.18(1.3)	81.56(1.3)	1.15(1.5)	4.24(1.5)
24	36.02(1.1)	84.25(1.3)	1.59(1.4)	7.64(1.4)
32	46.56(1.2)	86.75(1.1)	1.96(1.5)	11.09(1.5)
40	57.58(1.0)	90.52(1.0)	2.04(1.4)	15.64(1.3)
48	66.32(0.5)	93.42(0.5)	2.56(1.4)	18.97(1.2)

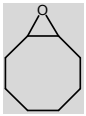
[a]Reaction conditions: ZnS-N/C nanocomposites (0.05 g), *cis*-cyclooctene (10 mL), TBHP (0.5 mL), 80°C, under O_2 and N_2 atmosphere with visible light irradiation, respectively.

Table S6. The effect of reaction time on selective oxidation of *cis*-cyclooctene with error under dark with Zn-N/C nanocomposites as catalyst.[a]

Reaction time (h)	Product Selectivity (%)		Conversion (%)	$\Sigma_{sel}C_8$[b]
				
0	0	0	0	0
8	77.02(1.3)	13.09(1.4)	2.03(1.4)	99.75(1.2)
16	80.49(1.3)	10.58(1.3)	4.24(1.4)	99.59(1.3)
24	83.28(1.2)	8.93(1.4)	7.64(1.3)	99.45(1.2)
32	84.92(1.2)	7.56(1.4)	11.09(1.2)	99.37(1.2)
40	87.36(1.3)	6.65(1.5)	15.64(1.2)	99.12(1.4)
48	89.57(1.3)	5.24(1.5)	18.97(1.2)	98.89(1.4)

[a]Reaction conditions: ZnS-N/C nanocomposites (0.05 g), *cis*-cyclooctene (10 mL), TBHP (0.5 mL), 80°C, under dark. [b]Total selectivity to C_8 partial oxidation products.

Table S7. The effect of reaction time on selective oxidation of *cis*-cyclooctene with error under visible light irradiation by using the physical mixture of ZnS and N-doped carbon as catalyst.[a]

Reaction time (h)	Physical mixture of ZnS and N-doped carbon	
	Conversion (%)	Product selectivity (%) 
0	0	0
8	1.23(1.4)	13.67(1.4)
16	3.75(1.4)	14.95(1.3)
24	7.89(1.3)	11.73(1.3)
32	11.37(1.2)	10.26(1.2)
40	13.53(1.1)	8.76(1.2)
48	25.74(1.0)	4.32(1.4)

[a]Reaction conditions: materials of ZnS and N-doped carbon (0.05 g), *cis*-cyclooctene (10 mL), TBHP (0.5 mL), 80°C, under visible light irradiation. [b]Total selectivity to C_8 partial oxidation products.

Table S8 The electrochemical band gaps of ZnS-N/C nanocomposites, ZnS/C and N-doped carbon with the cyclic voltammetry (CV) method and the band gap of ZnS with reference S1.

Catalyst	Cyclic voltammetry		Band-gap/eV
	HOMO/eV	LUMO/eV	
ZnS-N/C	-6.18	-4.37	1.81
ZnS/C	-6.05	-4.57	1.48
N-doped carbon	-5.76	-4.74	1.02
ZnS	-	-	3.68[S1]

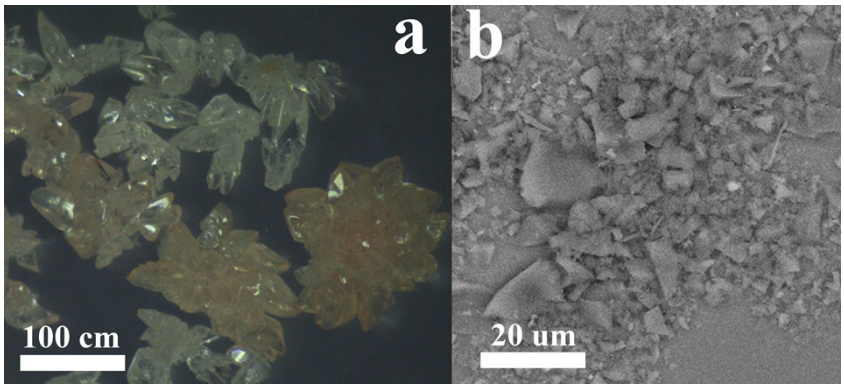


Fig. S1 (a) The photo of **L-1** (white) and **D-1** (orange). (b) SEM image of ZnS-N/C nanocomposites.

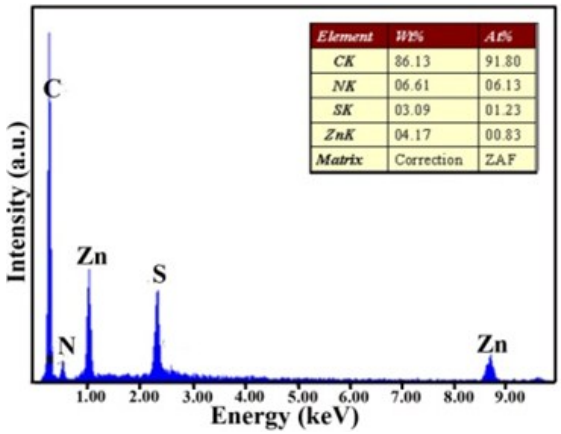


Fig. S2 EDS spectrum of ZnS-N/C nanocomposites.

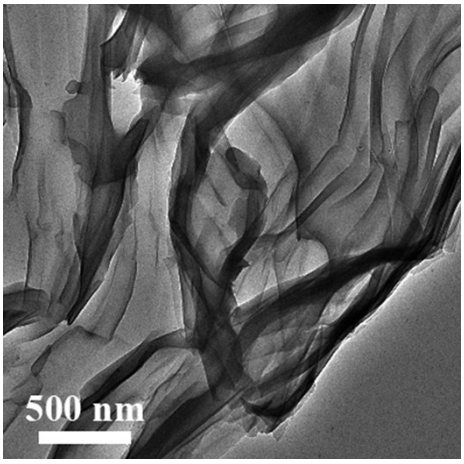


Fig. S3 TEM image of N-doped carbon.

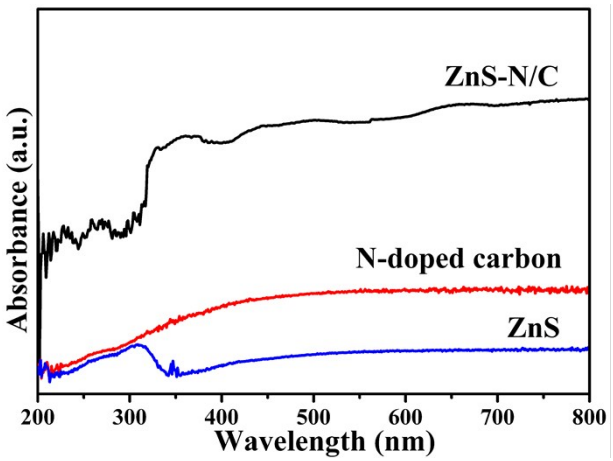


Fig. S4 UV-vis absorption spectra of ZnS-N/C nanocomposites, N-doped carbon and ZnS (black, red and blue traces, respectively).

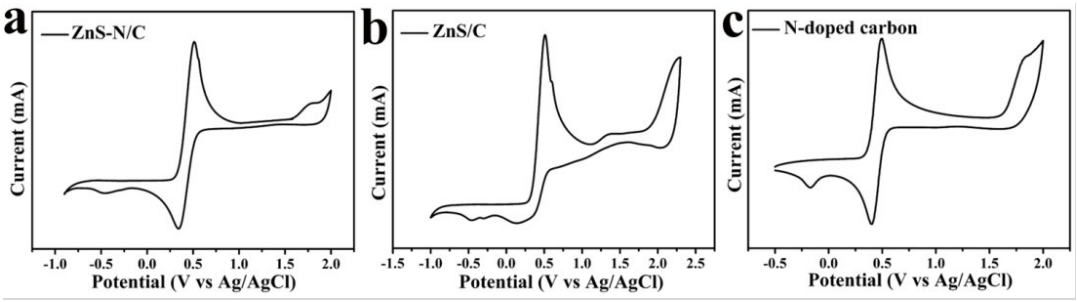


Fig. S5 CV curves of ZnS-N/C nanocomposites (a), ZnS /C (b) and N-doped carbon (c).

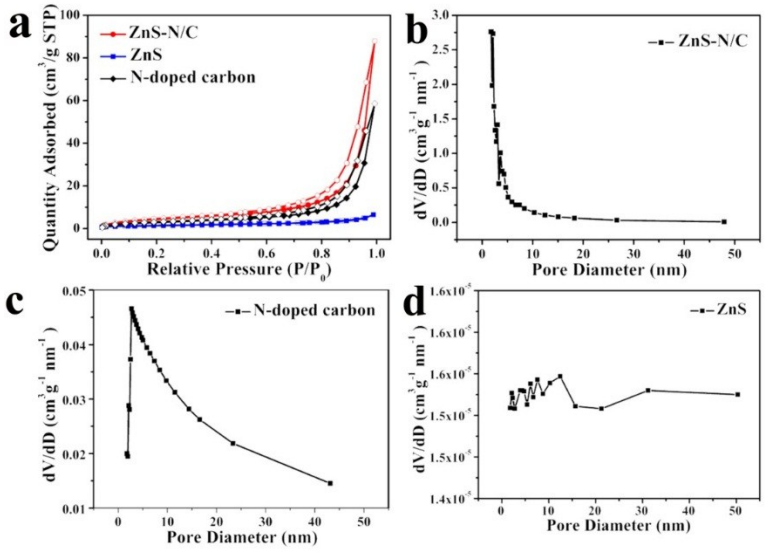


Fig. S6 (a) Nitrogen adsorption-desorption isotherms of ZnS-N/C nanocomposites, ZnS and N-doped carbon. (b, c and d) pore size distributions of ZnS-N/C nanocomposites, N-doped carbon and ZnS, respectively.

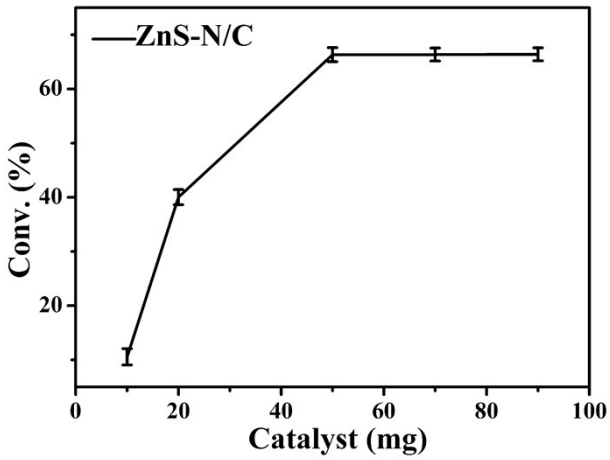


Fig. S7 The relationship between the conversion and the concentration of ZnS-N/C nanocomposites.

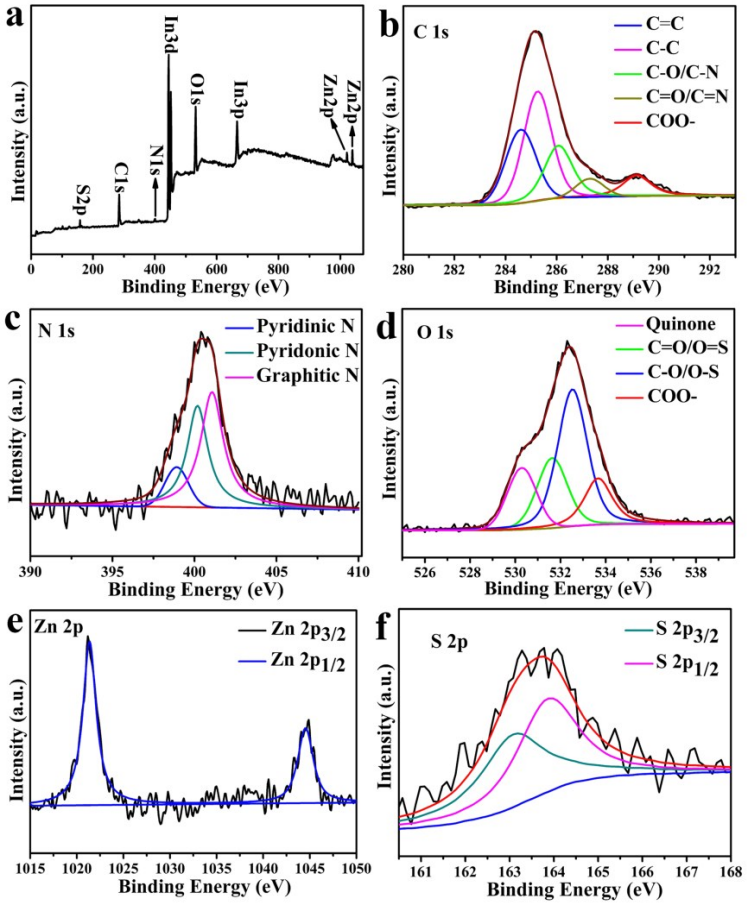


Fig. S8 XPS spectra of the as-obtained sample after catalytic reaction.

The full XPS survey spectrum in Fig. S7a shows that the sample contains C, N, O, Zn and S elements without other impurities. The C 1s XPS spectrum is shown in Fig. S7b, which can be divided into five peaks at 284.60, 285.25, 286.09, 287.32 and 289.15 eV, corresponding to C=C, C-C, C-O/C-N, C=O/C=N and COO-, respectively.[S2] The N 1s spectrum is shown in Fig. S7c, in which the peaks at 398.85, 400.14 and 401.08 eV attribute to the pyridinic, pyridonic and graphitic nitrogen species, respectively.[S3] The O 1s XPS spectrum in Fig. S7d shows for peaks at 530.30, 531.65, 532.54 and 533.67 eV, which are attributed to quinone, C-O/O-S, C=O/O=S, and COO-,

respectively.[S4] Fig. S7e shows the XPS spectrum of Zn 2p. The two peaks at 1022.33 and 1045.76 eV correspond to the Zn $2p_{3/2}$ and Zn $2p_{1/2}$, which is assigned to Zn^{2+}.[S5] Fig. S7f shows the S 2p XPS spectrum with peaks located at 162.32 and 163.41 eV for S $2p_{3/2}$ and S $2p_{1/2}$, respectively, which are characteristic of S^{2-} in the ZnS phase.[S5]

References

1 P. E. Lippens, M. Lannoo, *Phys. Rev. B*, 1989, **39**, 10935.

2 L. B. Tang, R. B. Ji, X. K. Cao, J. Y. Lin, H. X. Jiang, X. M. Li, K. S. Teng, C. M. Luk, S. J. Zeng, J. H. Hao, S. P. Lau, *ACS nano*, 2012, **6**, 5102.

3 G. D. Yang, Z. Jiang, H. H. Shi, T. C. Xiao, Z. F. Yan, *J. Mater. Chem*., 2010, **20**, 5301.

4 W. L. Li, Y. P. Hu, E. Rodíıguez-Castellón, T. J. Bandosz, *J. Mater. Chem. A*, 2017, **5**, 16315.

5 X. Yang, H. T. Xue, J. Xu, X. Huang, J. Zhang, Y. B. Tang, T. W. Ng, H. L. Kwong, X. M. Meng, C. S. Lee, *ACS Appl. Mater. Interfaces*, 2014, **6**, 9078.