Supporting Information

Defects Enriched N-doped Carbon Nanoflakes as Robust Carbocatalysts for H_2S Selective Oxidation

Shiyan Li,[a,b,#] Qingqing Gu,[a,#] Ning Cao,[b] Qian Jiang,[a] Chi Xu,[a,b] Chengfa Jiang,[b] Congmei Chen[c] Cuong Pham-Huu,[d] Yuefeng Liu[a,*]

[a] *Dalian National Laboratory for Clean Energy (DNL), Dalian Institute of Chemical Physics, Chinese Academy of Science,457 Zhongshan Road, 116023 Dalian, China*

[b] *School of Chemical Engineering, Sichuan University, 610065, Chengdu, China*

[c] *National Supercomputing Center in Shenzhen (Shenzhen Cloud Computing Center), 518055, Shenzhen, China*

[d] *Institute of Chemistry and Processes for Energy, Environment and Health (ICPEES), UMR 7515 CNRS-University of Strasbourg, 25 rue Becquerel, 67087 Strasbourg Cedex 02, France*

# These authors contributed equally.

* Corresponding authors E-mail: yuefeng.liu@dicp.ac.cn (Y. Liu)

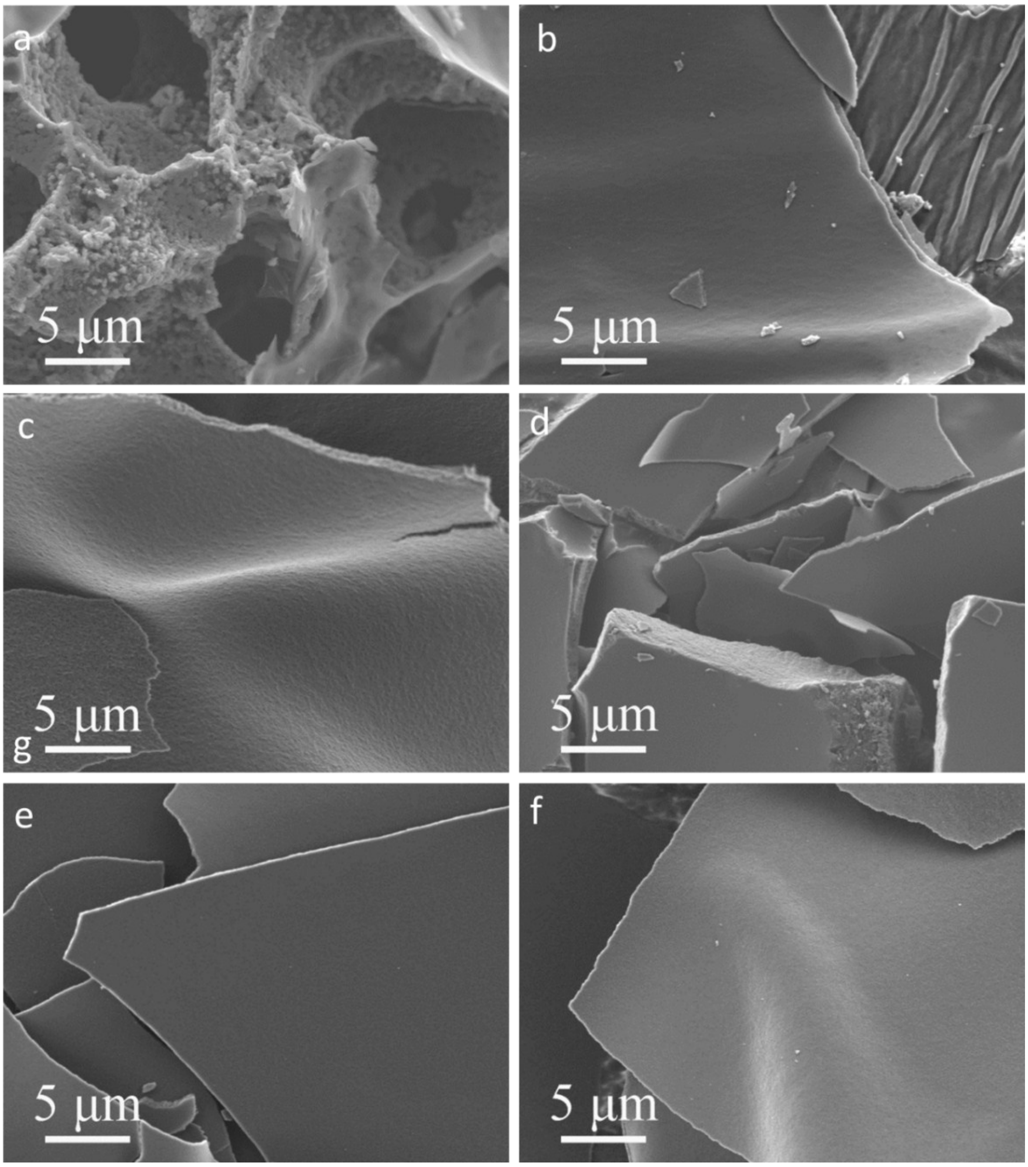

Figure S1. SEM images of the N-doped carbon nanoflakes: (a) EM-0-800, (b) EM-2-800, (c) EM-5-800, (d) EM-3.5-700, (e) EM-3.5-900, (f) EM-3.5-1000

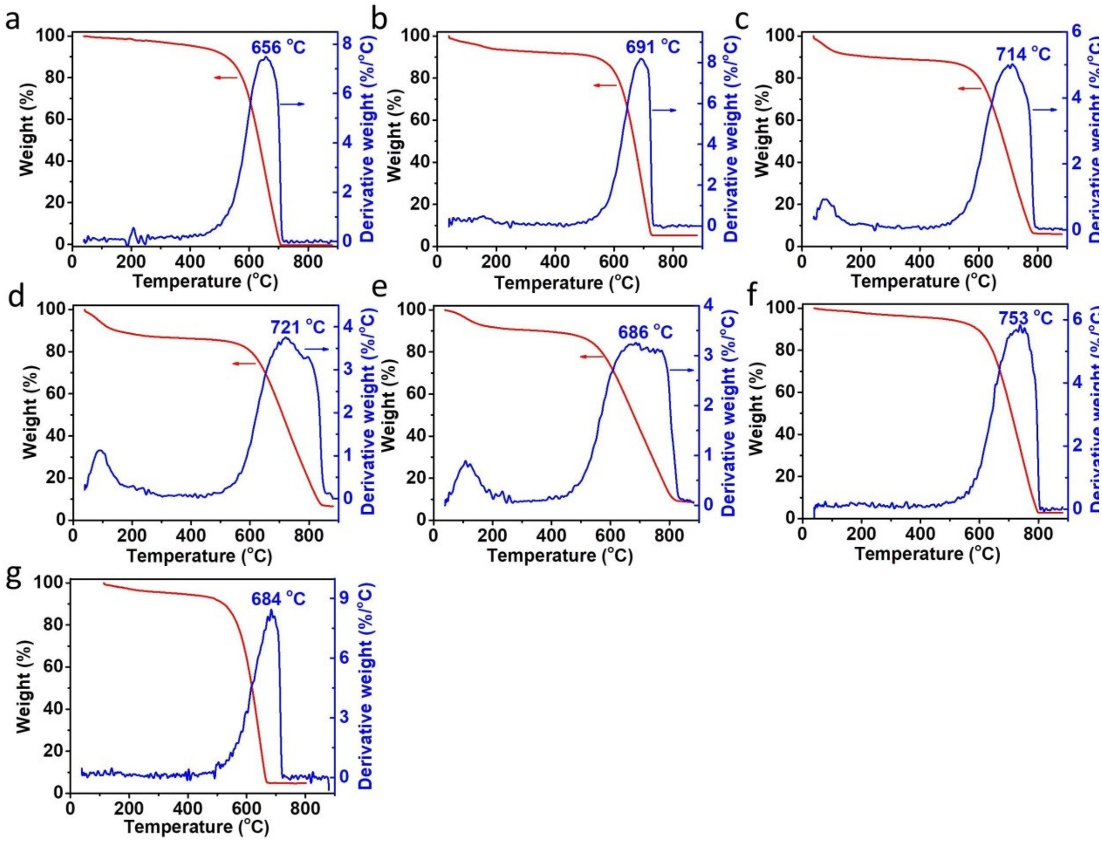

Figure S2. Thermal stability of N-doped carbon nanoflakes under air: (a) EM-0-800, (b) EM-2-800, (c) EM-3.5-800, (d) EM-5-800, (e) EM-3.5-700, (f) EM-3.5-900, (g) EM-3.5-1000

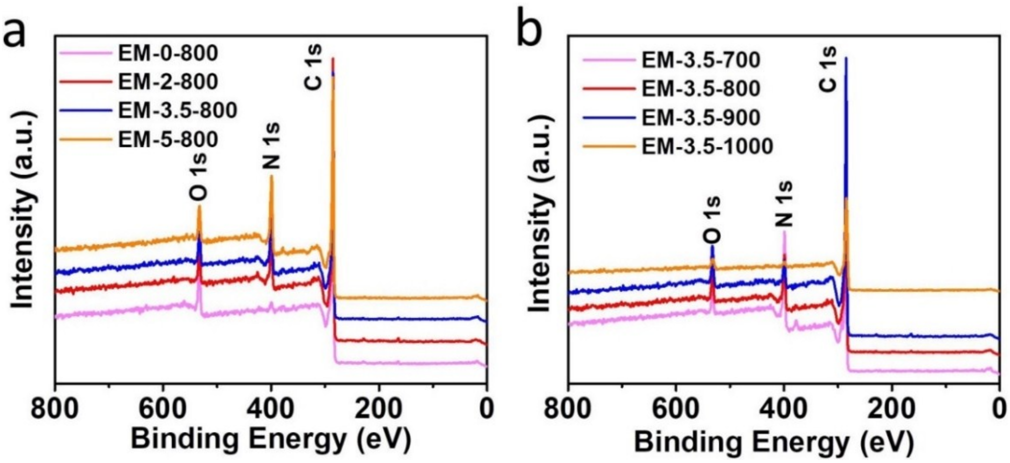

Figure S3. XPS survey scan of the N-doped carbon nanoflakes with (a) different melamine dosage and (b) different pyrolysis temperature.

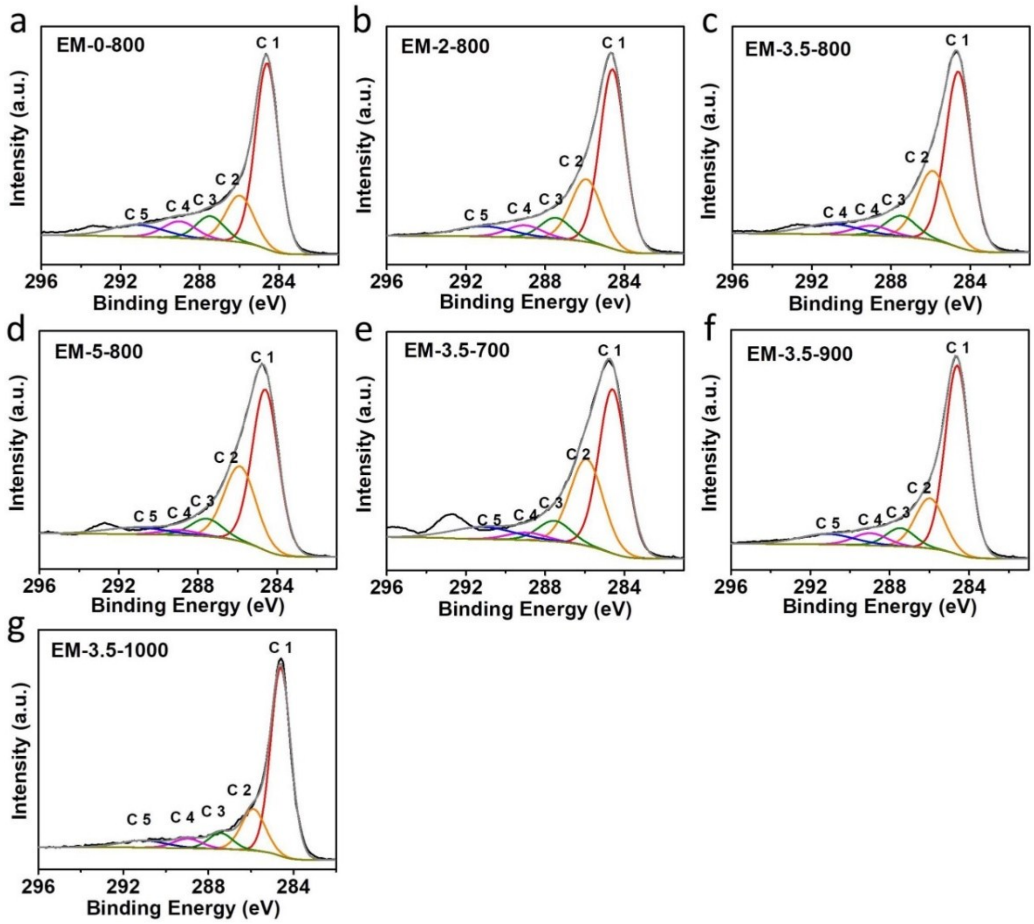

Figure S4. C1s high resolution XPS spectra of N-doped carbon nanoflakes.

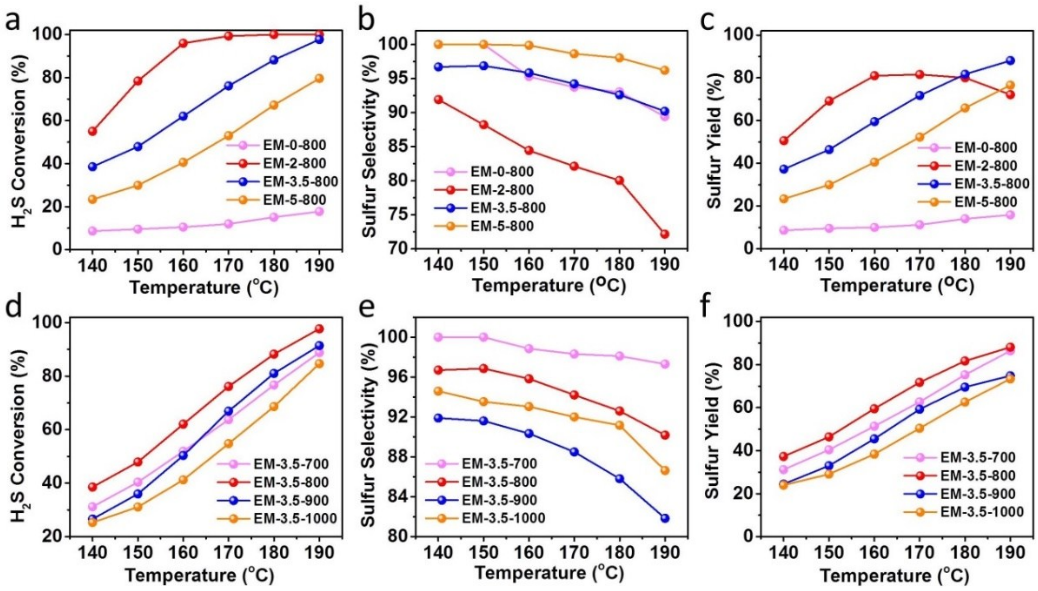

Figure S5. Effect of reaction temperature on (a, d) H_2S conversion, (b, e) sulfur selectivity, and (c, f) sulfur yield over N-doped carbon nanoflakes. Reaction condition: WHSV = 0.9 h^{-1}, O_2-to-H_2S molar ratio = 2.5, and steam concentration = 30 vol %.

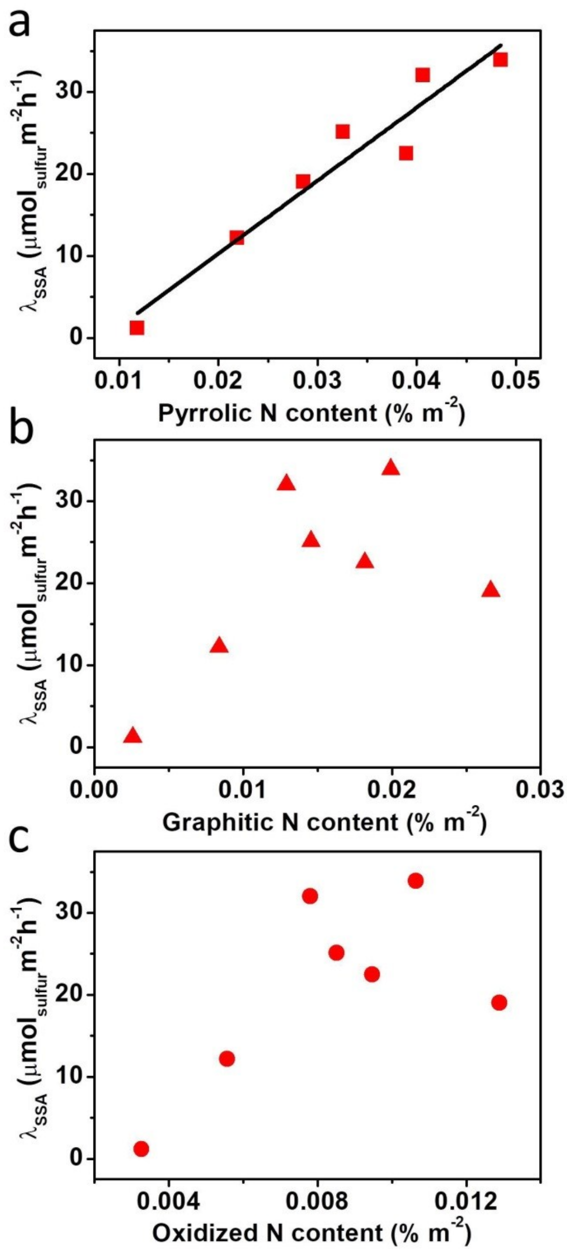

Figure S6. Relationship between sulfur formation rate (λ_{SSA}) and (a) pyrrolic N content, (b) graphitic N content, (c) oxidized N content in N-doped carbon nanoflakes.

Table S1. Textural properties and XPS characterization of the N-doped carbon nanoflakes

Sample[a]	S_{BET} m^2g^{-1}	S_{micro} m^2g^{-1}	V_T cm^3g^{-1}	V_{micro} cm^3g^{-1}	D nm	XPS analysis (at.%) C	O	N	N/C	λ_{SSA}, $\mu mol_{sulfur}m^{-2}h^{-1}$
EM-0	3530	-	1.99	-	3.1	87.1	10.2	2.7	0.03	1.2
EM-2	1585	402	0.75	0.19	3.2	84.0	6.3	9.7	0.12	12.2
EM-3.5	941	296	0.59	0.14	3.2	78.1	5.7	16.2	0.21	25.1
EM-5	605	348	0.26	0.17	2.5	74.2	6.2	19.6	0.26	33.9
EM-3.5-700	724	233	0.45	0.11	3.2	71.3	5.8	22.9	0.32	32.0
EM-3.5-900	891	298	0.51	0.14	3.1	86.7	7.1	6.2	0.07	22.5
EM-3.5-1000	1032	340	0.69	0.15	2.9	89.8	5.7	4.5	0.05	19.0

[a] Catalysts are denoted as EM-X-Y, where the X refers to the melamine dosage (from 0g to 5g), and the Y refers to the annealed temperature (from 700 to 1000 °C).

Table S2. C1s high resolution XPS spectra of N-doped carbon nanoflakes

Sample[a]	C at.%	C1 at.%	C2 at.%	C3 at.%	C4 at.%	C5 at.%
EM-0-800	87.1	50.6	15.3	7.6	6.3	7.3
EM-2-800	84.0	47.0	19.7	6.6	4.5	6.2
EM-3.5-800	78.1	42.8	20.3	6.1	3.3	5.6
EM-5-800	74.2	40.5	22.6	5.3	1.8	4.0
EM-3.5-700	71.3	35.3	22.4	5.3	2.3	6.0
EM-3.5-900	86.7	52.5	16.7	6.1	4.7	6.7
EM-3.5-1000	89.8	58.9	15.6	6.0	4.2	5.1

Table S3. The DFT results of binding energy and Mulliken charge analysis

N species	binding energy eV	Δq_C e	Δq_S e
graphene edge	-2.02	-0.09	-0.09
Pyrid-N	-2.89	-0.06	-0.13
Grap-N	-2.80	-0.03	-0.09
Oxid-N	-1.98	-0.02	-0.08

Table S4. Comparison of desulfurization performance at temperatures above dew-point temperature (>180 ^oC) of sulfur over different desulfurization catalysts reported in the literature

Catalysts	T, ^oC	H_2S, vol.%	O_2, vol.%	WHSV, h^{-1}	X_{H2S} (%)	S_S (%)	$\lambda_{cat.}$, $g_{sulfur}kg_{cat.}^{-1}h^{-1}$	Ref.
EM-3.5-800	190	1	2.5	0.9	97.7	90.2	755	this work
EM-3.5-700	190	1	2.5	0.9	88.8	97.3	741	this work
EM-5-800	190	1	2.5	0.9	79.6	96.2	656	this work
N-C/CNT450 700	190	1	2.5	0.6	94.6	84.2	455	1
N-C/CNT450 800	190	1	2.5	0.6	99.4	79.2	449	1
N-C/CNT450 900	190	1	2.5	0.6	100	72.0	412	1
N-C/CNT400 800	190	1	2.5	0.6	91.4	84.6	442	1
N-OMCS-700	190	0.5	0.25	12000 ($ml\cdot g^{-1}\cdot h^{-1}$)	100	91	156	2
PCNUC5	210	0.25	0.5	3000 ($ml\cdot g^{-1}\cdot h^{-1}$)	100	97.5	42	3
CNM-600	180	0.5	0.25	3000 ($ml\cdot g^{-1}\cdot h^{-1}$)	≈ 96	≈ 97	40	4
N@CF-800	230	1	2.5	0.6	57	95	306	5
$^{A}N@C/SiC_{E}^{2}$	210	1	2.5	0.3	> 97	70	383	6
O-CNT-250-24	190	1	2.5	0.6	50	90	254	7
N-CNT/SiC foam	190	1	2.5	0.72	99.8	75	113	8
N-CNT	190	1	2.5	0.32	91	75	205	8
N-CNT/SiC	190	1	2.5	0.32	95.8	74.1	100	9
N-CNT beads	210	1	2.5	0.3	99.1	61.6	47	10
OGFs-16	250	1	2.5	0.1	98	86	79	11
γ -Al_2O_3	240	0.5	0.25	10500 ($ml\cdot g^{-1}\cdot h^{-1}$)	100	93	140	12
CeO_2-R	220	0.5	0.25	10500 ($ml\cdot g^{-1}\cdot h^{-1}$)	100	100	150	13
CUS-MIL-100(Fe)	190	0.5	0.25	6400 (GHSV)	100	100	171	14
TiO_2-CNT16%	200	0.44	0.22	35000 (GHSV)	98.3	99.5	84	15

References

1. S. Li, Y. Liu, H. Gong, K.-H. Wu, H. Ba, C. Duong-Viet, C. Jiang, C. Pham-Huu and D. Su, *ACS Appl. Nano Mater.*, 2019, **2**, 3780-3792.
2. X. Kan, X. Chen, W. Chen, J. Mi, J.-Y. Zhang, F. Liu, A. Zheng, K. Huang, L. Shen, C. Au and L. Jiang, *ACS Sustain. Chem. Eng.*, 2019, **7**, 7609-7618.
3. G. Lei, Z. Dai, Z. Fan, X. Zheng, Y. Cao, L. Shen, Y. Xiao, C. Au and L. Jiang, *Carbon*, 2019, **155**, 204-214.
4. L. Shen, G. Lei, Y. Fang, Y. Cao, X. Wang and L. Jiang, *Chem. Commun.*, 2018, **54**, 2475-2478.
5. Y. Liu, C. Duong-Viet, J. Luo, A. Hébraud, G. Schlatter, O. Ersen, J.-M. Nhut and C. Pham-Huu, *ChemCatChem*, 2015, **7**, 2957-2964.
6. H. Ba, Y. Liu, L. Truong-Phuoc, C. Duong-Viet, X. Mu, W. H. Doh, T. Tran-Thanh, W. Baaziz, L. Nguyen-Dinh, J.-M. Nhut, I. Janowska, D. Begin, S. Zafeiratos, P. Granger, G. Tuci, G. Giambastiani, F. Banhart, M. J. Ledoux and C. Pham-Huu, *Chem. Commun.*, 2015, **51**, 14393-14396.
7. C. Duong-Viet, Y. Liu, H. Ba, L. Truong-Phuoc, W. Baaziz, L. Nguyen-Dinh, J.-M. Nhut and C. Pham-Huu, *Appl. Catal. B: Environ.*, 2016, **191**, 29-41.
8. K. Chizari, A. Deneuve, O. Ersen, I. Florea, Y. Liu, D. Edouard, I. Janowska, D. Begin and C. Pham-Huu, *ChemSusChem*, 2012, **5**, 102-108.
9. C. Duong-Viet, H. Ba, Y. Liu, L. Truong-Phuoc, J.-M. Nhut and C. Pham-Huu, *Chinese J. Catal.*, 2014, **35**, 906-913.
10. H. Ba, C. Duong-Viet, Y. Liu, J.-M. Nhut, P. Granger, M. J. Ledoux and C. Pham-Huu, *C. R. Chim.*, 2016, **19**, 1303-1309.
11. Z. Xu, C. Duong-Viet, H. Ba, B. Li, T. Truong-Huu, L. Nguyen-Dinh and C. Pham-Huu, *Catalysts*, 2018, **8**, 145.
12. L. Shen, X. Zheng, G. Lei, X. Li, Y. Cao and L. Jiang, *Chem. Eng. J.*, 2018, **346**, 238-248.
13. X. Zheng, Y. Li, L. Zhang, L. Shen, Y. Xiao, Y. Zhang, C. Au and L. Jiang, *Appl. Catal. B: Environ.*, 2019, **252**, 98-110.
14. X. Zheng, L. Zhang, Z. Fan, Y. Cao, L. Shen, C. Au and L. Jiang, *Chem. Eng. J.*, 2019, **374**, 793-801.
15. M. Daraee, M. Baniadam, A. Rashidi and M. Maghrebi, *Chem. Phys.*, 2018, **511**, 7-19.