Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Revealing Structure–Activity Links in Hydrazine Oxidation: Doping and Nanostructure in Carbide-Carbon Electrocatalysts

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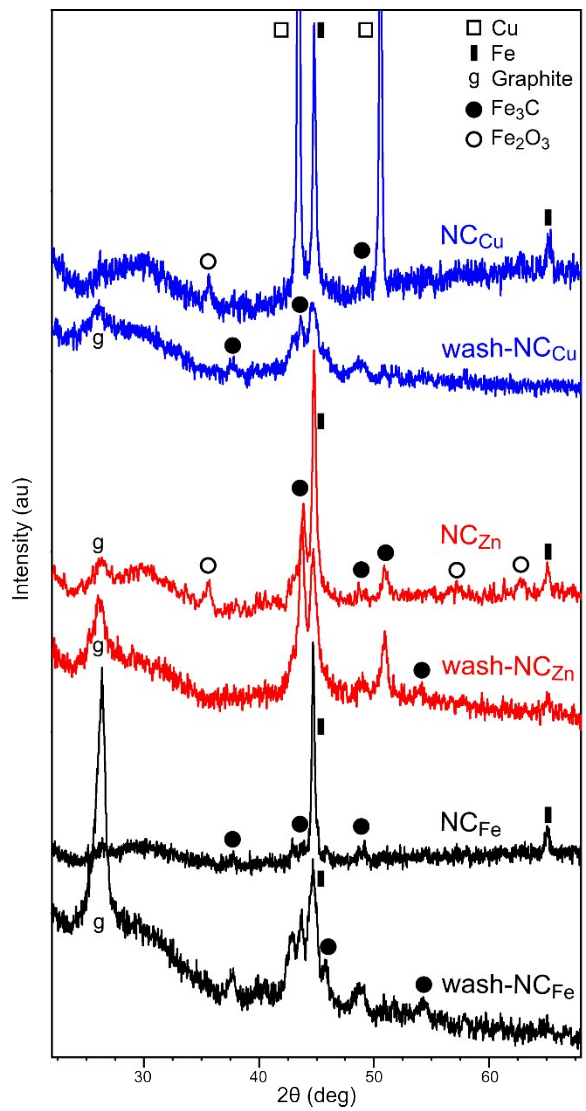

Figure S1. X-ray diffractograms of NCM and wash-NCM (M = Cu, Zn, Fe).

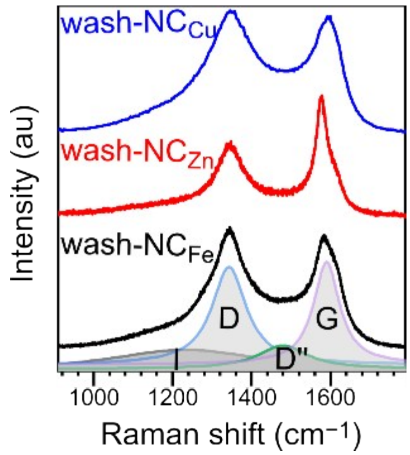

Figure S2. Raman spectra of wash-NC$_M$ (M=Cu, Zn, Fe), with deconvolution demonstrated for wash-NC$_{Fe}$.

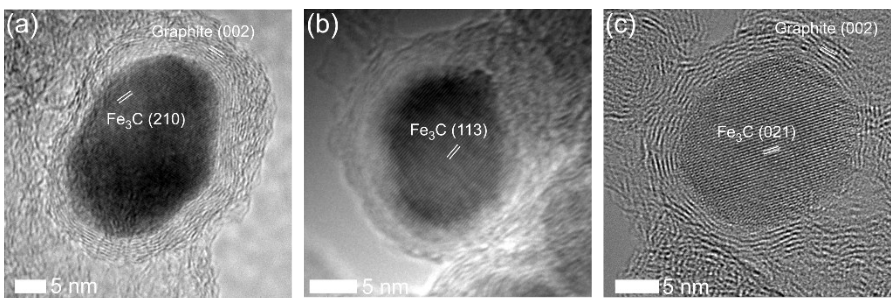

Figure S3. HRTEM images with crystalline Miller indices, analysed by d-spacing for (a) wash-NC$_{Fe}$ (b) wash-NC$_{Zn}$ (c) wash-NC$_{Cu}$

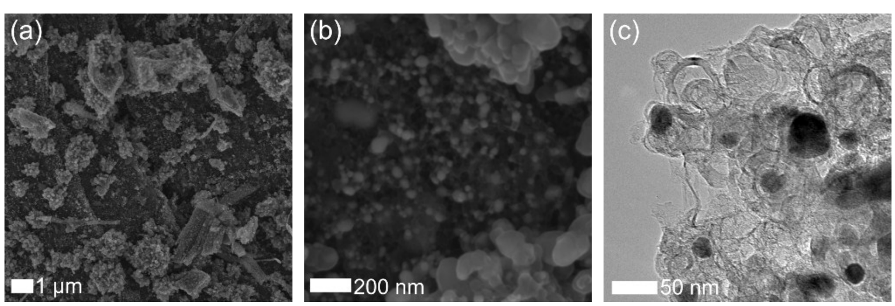

Figure S4. (a) HRSEM of wash-NC$_{Fe}$, x10K. (b) HRSEM of wash-NC$_{Fe}$, x200K. (c) HRTEM of wash-NC$_{Fe}$.

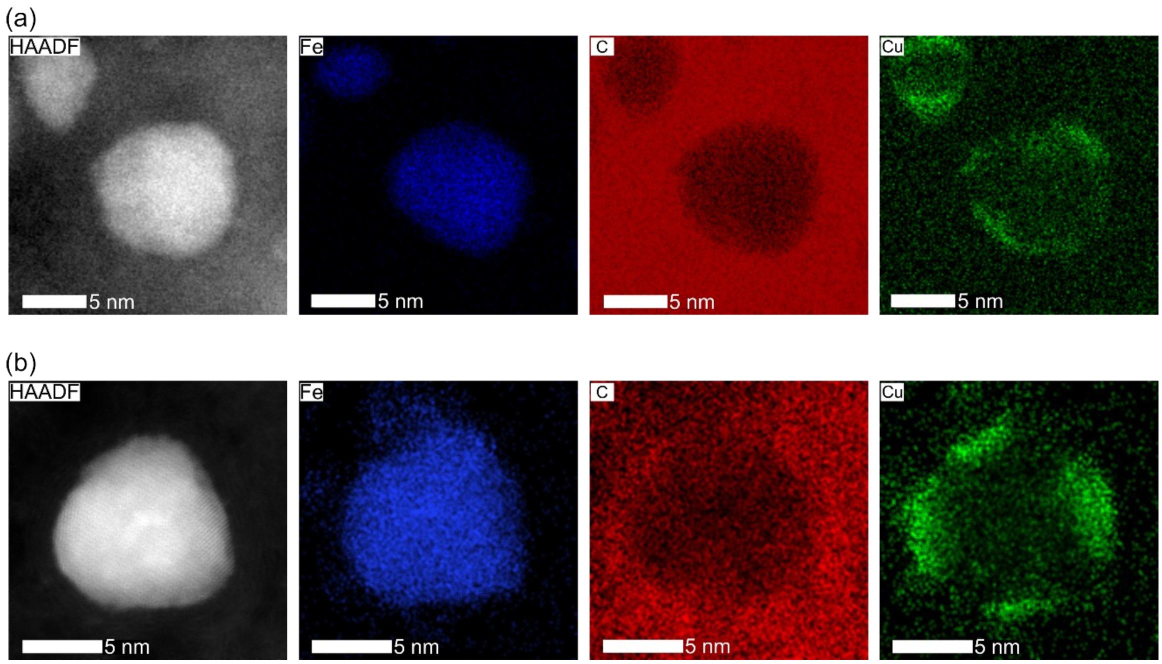

Figure S5. Single-particle elemental mapping images of (a) NC_{Cu}; (b) wash-NC_{Cu}.

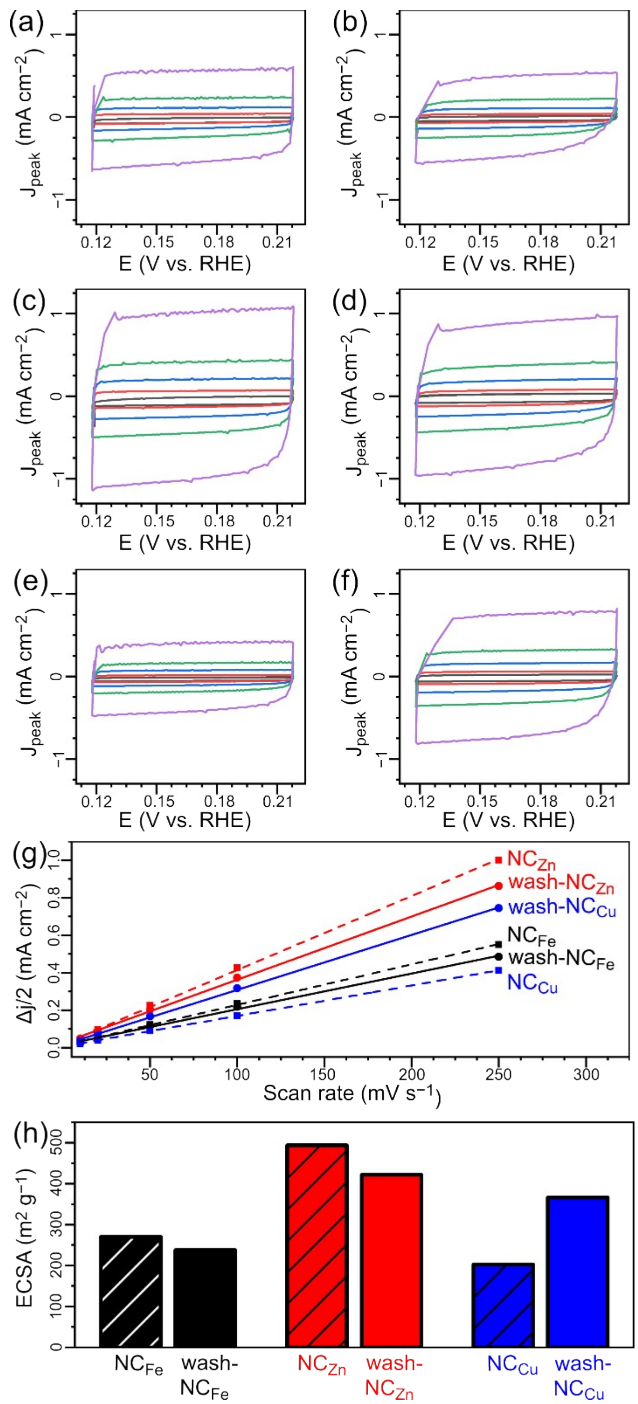

Figure S6. CV of pure double-layer charging (no N_2H_4) of (a) NC_{Fe} (b) wash-NC_{Fe} (c) NC_{Zn} (d) wash-NC_{Zn}. (e) NC_{Cu} (f) wash-NC_{Cu}. (g) Double-layer charging vs. scan rate at 0.168 V vs. RHE. (h) Electrochemical surface area (ECSA) before and after washing. NC_{Fe} and NC_{Zn} show similar ECSA after washing, while NC_{Cu} has a near two-fold increase. The trends are similar to SSAs derived from N_2 porosimetry (Figure 7), except for the increase in SSA in NC_{Fe} after washing, possibly arising from micropores accessible to N_2 yet not to solution. The large differences between BET SSA and ECSA values are due to multi-layer charging in ECSA experiments, while BET SSA is calculated for a single N_2 monolayer.

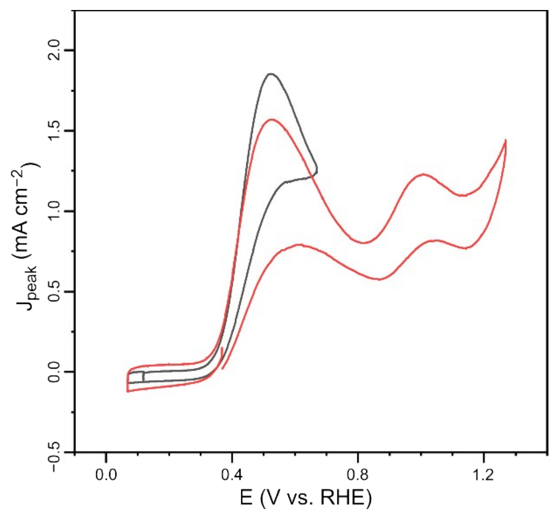

Figure S7. CV of HzOR on wash-NC_{Fe} at extended potential range. 20 mM N_2H_4, 1M KOH, 10 mV s^{-1}.

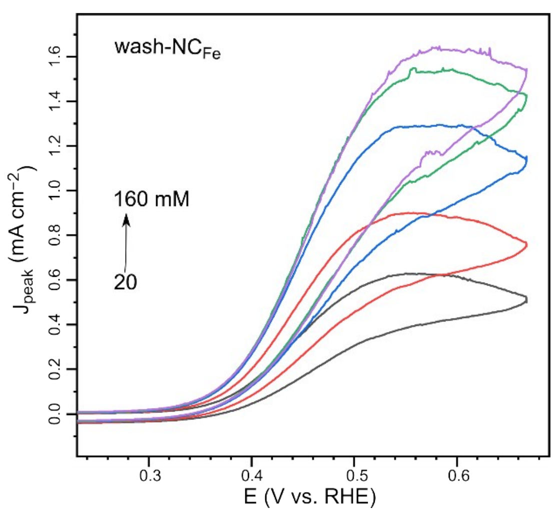

Figure S8. CV of HzOR on wash-NC_{Fe} at varied N_2H_4 concentrations on wash-NC_{Fe}. 1M KOH, [20, 40, 80, 100, 160 mM], 10 mV s^{-1}.

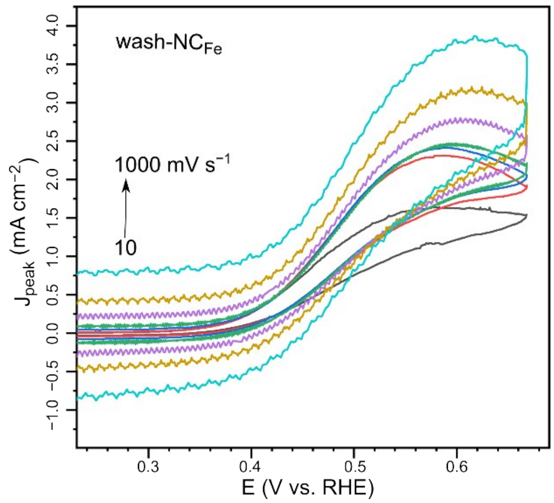

Figure S9. Cyclic voltammetry of HzOR at varied scan rates on wash-NC$_{Fe}$. 1M KOH, [10, 20, 50, 100, 250, 500, 1000 mV s^{-1}], 160 mM N_2H_4.

Catalyst	Electrolyte	E_{onset} vs. RHE	Ref.
wash-NC_M (M=Cu, Zn, Fe)	**1 M KOH**	**0.28**	**This work**
Cu_3P on Cu foam	1 M KOH	0.00	[1]
FeP on Ni foam	1 M KOH	0.00	[2]
Fe_2MoC on NC	1 M KOH	0.28	[3]
Metal-free, alkaline-earth-derived NC	1 M KOH	0.34	[4]
'Tree-bark'-structured NC	1 M KOH	0.40	[5]
Fe_2O_3 on C	1 M KOH	0.50	[6]
Cu on graphene	0.1 M KOH	0.55	[7]
Graphene 'nano-hills'	0.1 M KOH	0.64	[8]
Cu NPs on C	0.1 M KOH	0.71	[9]
Cu cubes on graphene	0.1 M KOH	0.81	[10]
Fe@Cu-P on C	0.1 M KOH	0.81	[11]
CuO nanoshapes on C	0.1 M KOH	0.86	[12]
CuO nanocrystals on C	0.1 M KOH	0.91	[13]
Ni- or Co-based			
NiCo pompoms	1 M KOH	-0.19	[14]
$Ni_{60}Co_{40}$ on C	1 M KOH	-0.15	[15]
NiZn on C	1 M KOH	-0.10	[16]
$Ni_{0.5}Co_{0.5}Se_2$ on C	1 M KOH	-0.10	[17]
Ni–B film	1 M NaOH	-0.09	[18]
NiMo on C	1 M KOH	-0.08	[19]
NiMn, NiFe, NiZn on C	1 M KOH	-0.05	[20]
Ni_2P array	1 M KOH	-0.05	[21]
Ni-Zn on GO	1 M NaOH	-0.05	[22]
CoP on Ti mesh	1 M KOH	-0.05	[23]
Co@CoO	1 M KOH	-0.03	[24]
Ni NPs on C	0.1 M NaOH	0.00	[25]
Ni-B on C	1 M KOH	0.00	[26]
Ni-Zn on Ni foam	1 M NaOH	0.00	[27]
$NiCoSe_2$ on Ni foam	0.5 M KOH	0.31	[28]
Ni_3S_2 on Ni foam	0.1 M KOH	0.86	[29]
Co-Mo alloys	1 M NaOH	0.90	[30]
Noble metal-based			
Pd-Rh on NC	1 M KOH	-0.03	[31]
Pt-NiO_x on C	1 M NaOH	0.00	[32]
Pd on Ni foam	1 M NaOH	0.00	[33]
Ag on g-C_3N_4	0.1 M NaOH	0.51	[34]
Ag on Zn-based MOF	0.1 M NaOH	0.61	[35]
Au on TiO_2	0.1 M KOH	0.70	[36]
Cu-Pd-O_x	0.1 M KOH	0.9	[37]

Table S1. HzOR electrocatalysis at alkaline pH. Catalysts that are non-supported on a carbon matrix are grouped separately and colored grey, since carbon supports are useful for dispersion, support, and conductivity enhancement of the catalysts (aspects not expressed by the onset potential). C and NC stand for carbon and nitrogen-doped carbon, respectively.

Material	C at%	N at%	O at%	Fe at%	M at% (=Cu, Zn)
NC_{Fe}	89.9	1.7	7.3	1.1	
wash-NC_{Fe}	95.3	1.6	2.6	0.5	
NC_{Zn}	90.4	3.1	5.7	0.8	0
wash-NC_{Zn}	92.9	3.1	3.4	0.6	0
NC_{Cu}	86.3	2.1	8.2	1.7	1.6
wash-NC_{Cu}	84.2	1.9	10.8	1.4	1.4

Table S2. XPS results for NC_M and wash-NC_M (M=Cu, Zn, Fe). The values are within ±0.4%, based on peak integration error.

References:

1 M. Liu, R. Zhang, L. Zhang, D. Liu, S. Hao, G. Du, A. M. Asiri, R. Kong and X. Sun, *Inorg. Chem. Front.*, 2017, **4**, 420–423.

2 L. Zhang, D. Liu, S. Hao, L. Xie, F. Qu, G. Du, A. M. Asiri and X. Sun, *Chem. Sel.*, 2017, **2**, 3401–3407.

3 K. Ojha, E. M. Farber, T. Y. Burshtein and D. Eisenberg, *Angew. Chem. Int. Ed.*, 2018, **57**, 17168–17172.

4 K. Ojha, W. Stroek, E. M. Farber, T. Y. Burshtein, S. Arustamian, L. Hasson, M. Ferbinteanu, S. Tanase and D. Eisenberg, 2019, submitted.

5 J. Jeong, M. Choun and J. Lee, *Angew. Chem. Int. Ed.*, 2017, **56**, 13513–13516.

6 Y. Wang, Z. Chen, H. Wu, F. Xiao, E. Cao, S. Du, Y. Wu and Z. Ren, *ACS Sustain. Chem. Eng.*, 2018, **6**, 15727–15736.

7 F. He, L. Mi, Y. Shen, X. Chen, Y. Yang, H. Mei, S. Liu, T. Mori and Y. Zhang, *J. Mater. Chem. A*, 2017, **5**, 17413–17420.

8 K. Akbar, J. H. Kim, Z. Lee, M. Kim, Y. Yi and S.-H. Chun, *NPG Asia Mater.*, 2017, **9**, e378.

9 X. Gao, C. Du, C. Zhang and W. Chen, *ChemElectroChem*, 2016, **3**, 1266–1272.

10 H. Gao, Y. Wang, F. Xiao, C. B. Ching and H. Duan, *J. Phys. Chem. C*, 2012, **116**, 7719–7725.

11 Y. Wang, X. Liu, T. Tan, Z. Ren, Z. Lei and W. Wang, *J. Alloys Compd.*, 2019, **787**, 104–111.

12 Y. Ma, H. Li, R. Wang, H. Wang, W. Lv and S. Ji, *J. Power Sources*, 2015, **289**, 22–25.

13 Y. Ma, H. Wang, J. Key, S. Ji, W. Lv and R. Wang, *J. Power Sources*, 2015, **300**, 344–350.

14 H. Wang, Y. Ma, R. Wang, J. Key, V. Linkov and S. Ji, *Chem. Commun.*, 2015, **51**, 3570–3573.

15 J. Sanabria-Chinchilla, K. Asazawa, T. Sakamoto, K. Yamada, H. Tanaka and P. Strasser, *J. Am. Chem. Soc.*, 2011, **133**, 5425–5431.

16 A. Serov, M. Padilla, A. J. Roy, P. Atanassov, T. Sakamoto, K. Asazawa and H. Tanaka, *Angew. Chem.*, 2014, **126**, 10504–10507.

17 G. Wang, J. Chen, P. Cai, J. Jia and Z. Wen, *J. Mater. Chem. A*, 2018, **6**, 17763–17770.

18 X.-P. Wen, H.-B. Dai, L.-S. Wu and P. Wang, *Appl. Surf. Sci.*, 2017, **409**, 132–139.

19 T. Asset, A. Roy, T. Sakamoto, M. Padilla, I. Matanovic, K. Artyushkova, A. Serov, F. Maillard, M. Chatenet, K. Asazawa, H. Tanaka and P. Atanassov, *Electrochimica Acta*, 2016, **215**, 420–426.

20 T. Sakamoto, K. Asazawa, J. Sanabria-Chinchilla, U. Martinez, B. Halevi, P. Atanassov, P. Strasser and H. Tanaka, *J. Power Sources*, 2014, **247**, 605–611.

21 C. Tang, R. Zhang, W. Lu, Z. Wang, D. Liu, S. Hao, G. Du, A. M. Asiri and X. Sun, *Angew. Chem.*, 2017, **129**, 860–864.

22 Z. Feng, D. Li, L. Wang, Q. Sun, P. Lu, P. Xing and M. An, *J. Alloys Compd.*, 2019, **788**, 1240–1245.

23 J. Wang, R. Kong, A. M. Asiri and X. Sun, *ChemElectroChem*, 2017, **4**, 481–484.

24 X. Yan, Y. Liu, J. Lan, Y. Yu, J. Murowchick, X. Yang and Z. Peng, *Mater. Chem. Front.*, 2018, **2**, 96–101.

25 T.-Y. Jeon, M. Watanabe and K. Miyatake, *ACS Appl. Mater. Interfaces*, 2014, **6**, 18445–18449.

26 S. Lu, D. Cao, X. Xu, H. Wang and Y. Xiang, *RSC Adv.*, 2014, **4**, 26940–26945.

27 Z. Feng, D. Li, L. Wang, Q. Sun, P. Lu, P. Xing and M. An, *Electrochimica Acta*, 2019, **304**, 275–281.

28 K. Akbar, J. H. Jeon, M. Kim, J. Jeong, Y. Yi and S.-H. Chun, *ACS Sustain. Chem. Eng.*, 2018, **6**, 7735–7742.

29 X. Liu, Y. Li, N. Chen, D. Deng, X. Xing and Y. Wang, *Electrochimica Acta*, 2016, **213**, 730–739.

30 M. Abdolmaleki, A. Bodaghi, J. Hosseini and S. Jamehbozorgi, *J. Chin. Chem. Soc.*, 2018, **65**, 970–976.
31 G. Wang, S. Jing and Y. Tan, *Sci. Rep.*, 2017, **7**, 16465.
32 D. C. de Oliveira, W. O. Silva, M. Chatenet and F. H. B. Lima, *Appl. Catal. B Environ.*, 2017, **201**, 22–28.
33 L.-S. Wu, X.-P. Wen, H. Wen, H.-B. Dai and P. Wang, *J. Power Sources*, 2019, **412**, 71–77.
34 M. Afshari, M. Dinari and M. M. Momeni, *J. Electroanal. Chem.*, 2019, **833**, 9–16.
35 F. Asadi, S. N. Azizi and S. Ghasemi, *J. Mater. Sci. Mater. Electron.*, , DOI:10.1007/s10854-019-00834-y.
36 N. Roy, K. Bhunia, C. Terashima, A. Fujishima and D. Pradhan, *ACS Omega*, 2017, **2**, 1215–1221.
37 X.-Y. Zhang, S. Shi and H.-M. Yin, *ChemElectroChem*, 2019, **6**, 1514–1519.