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PAPER

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View Journal | View Issue Cite this: *J. Mater. Chem. A*, 2019, 7, 23098Selective surface functionalization generating site-isolated Ir on a MnO_x/N-doped carbon composite for robust electrocatalytic water oxidation†Ning Yan,^a Remko J. Detz,^{ab} Nitish Govindarajan,^a Jacobus M. Koelewijn,^a Bin Hua,^c Peng Li,^d Evert Jan Meijer^a and Joost N. H. Reek^{*,a}

Water oxidation catalysis plays a pivotal role in the context of the worldwide interest for sustainable energy. Finding cost-effective and robust catalysts to replace the state-of-the-art noble metal materials is hence urgent. In this work, we develop a molecular iridium complex that selectively and uniformly anchors on the surface of manganese oxide which is interconnected with a nitrogen-doped carbon forming a nanorod material. In the subsequent pyrolysis step, isolated Ir atoms are created on the manganese oxide surface and they strongly interact with the adjacent Mn. Through physicochemical characterization and computational studies, we demonstrate that the incorporation of Ir single-atom species in the MnO_x/N–C composite promotes the electrochemical water oxidation catalysis. The new material shows excellent activity in the oxygen evolution reaction in 0.1 M KOH with an overpotential of 250 mV at 10 mA cm^{−2}. Importantly, compared to a sample conventionally prepared with H₂IrCl₆, the novel Ir–MnO_x/N–C catalyst not only is more efficient, but also demonstrates improved redox stability without suffering from Ir leaching. Our approach opens up new opportunities for the rational design of site-isolated materials for catalysis in the field of energy applications.

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1. Introduction

In the global context of pursuing a sustainable future, technologies to harvest renewable energy sources are rapidly deployed to decrease our dependency on fossil fuel usage.^{1,2} To date, most of such systems produce electricity driven by, for instance, solar, wind, hydro, or geothermal energy. The intermittency of most of these sources demands storage solutions that allow the use of these forms of energies at any desirable point in time.^{3–5} Electrocatalytic water splitting offers a solution to both challenges, in which it converts electrical energy into oxygen (O₂) and hydrogen (H₂), which serves as a fuel and feedstock for the chemical industry.^{6–10} To avoid unnecessary energy losses, the efficiency of the hydrogen and oxygen evolution reactions (HER and OER) has to be maximized. Compared to the two-electron-transfer HER process, the OER is more complex,¹¹ involving four proton-coupled-electron transfer

steps. As this reaction proceeds *via* several different intermediates, scaling relationships apply that complicate catalyst optimization. As a result, most OER catalysts now operate at relatively high overpotentials. Therefore, a rational catalyst design/synthesis and a deeper understanding of the catalysis mechanism are important to improve catalysis beyond the level of today's typical OER catalysts.

A good OER catalyst must display excellent intrinsic activity at low overpotential, be highly stable, have adequate electrical conductivity, a suitable pore structure and high surface area, possess plentiful active sites, and be affordable. Unfortunately, it is nearly impossible to achieve all these properties within a single-phase material and as such composite/hybrid catalyst systems are increasingly explored in this field.^{12–19} Typically, earth-abundant transition metal oxide materials have good OER activity and are cost-effective, yet the general poor conductivity limits their application. Coupling them with a carbon-based support ensures smooth electron transfer and is widely proven as an effective solution.^{13,15,18} The generated hybrid interphase may also enhance catalytic efficiency.¹⁷ Recently, it has been demonstrated that the incorporation of site-isolated/single-atom noble metals can boost the activity while minimizing the cost of the catalyst.^{20–24} Because of the extremely high surface free energy, these single atoms are intrinsically prone to agglomeration and/or ripening.^{25,26} Choosing an appropriate support with effective anchoring sites to stabilize such single atoms is therefore a grand challenge.^{26–28}

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Previously, we have designed a variety of OER catalysts based on transition metal oxides and molecular iridium carbene complexes which showed high reaction rates at low overpotential.^{29–32} For the complex implementation in devices, we also demonstrated its immobilization in carbon nanotubes *via* functionalizing with pyrene moieties.³³ Inspired by these supramolecular strategies and aiming for improving the stability of site-isolated catalysts, we herein report mononuclear Ir-complexes that can selectively anchor to the metal oxide of a typical OER composite catalyst comprising nitrogen-doped carbon (N-C) and MnO_x . To this end, a typical trimethoxysilane functional group was installed onto the complex. Grafting this complex followed by pyrolysis enables highly selective and uniform deposition of Ir atoms on MnO_x , providing a superior water oxidation catalyst material.

2. Results and discussion

A mononuclear Ir-complex (2), based on a strongly coordinated carbene ligand and containing a trimethoxysilane anchoring moiety, is prepared in two steps (Fig. 1). The compound is fully characterized by nuclear magnetic resonance (NMR) and high-resolution mass spectrometry (HR-MS) analysis. The solid state structure is also unambiguously confirmed by single-crystal X-ray diffraction (see Table S1, Fig. S1 and S2 in the ESI†). Ir-complex 2 is grafted on the $\text{MnO}_x/\text{N-C}$ hybrid nanorod that is prepared using our previously established method.³⁰ In addition to the previously reported advantages, the selection of this hybrid is also motivated by the excess oxygen and defects from MnO_x (see the Experimental details†), providing abundant anchoring sites on the surface to accommodate the single-site Ir species.²⁵ Besides, the surface of MnO_x is rich in terminal $-\text{OH}$ groups as confirmed by infrared spectroscopy, guaranteeing the covalent interaction with complex 2 *via* the silane unit. Such an assembly also prevents the stacking of complex 2 on the substrate. The pentamethylcyclopentadienyl ligand (Cp^*) at the Ir metal center provides excellent stability during the grafting process;^{9,31,32} the large size of the complex results in a natural separation of the iridium atoms on the surface. To completely decompose the organic parts, a final pyrolysis step is carried out using a rapid heating/cooling cycle in N_2 to obtain the *ca.* 0.38 wt% site-isolated Ir atoms (hereafter denoted as Ir- $\text{MnO}_x/\text{N-C}$). For comparison, we have also prepared a control (hereafter denoted as C-Ir- $\text{MnO}_x/\text{N-C}$) using the conventional wet impregnation approach starting from H_2IrCl_6 . It is anticipated that the Ir will also atomically

Fig. 2 The schematic procedures of preparing Ir- $\text{MnO}_x/\text{N-C}$ and C-Ir- $\text{MnO}_x/\text{N-C}$; single Ir atoms are selectively deposited on the surface of MnO_x in the Ir- $\text{MnO}_x/\text{N-C}$ hybrid.

disperse, but on the surface of both N-C and MnO_x (*vide infra*).³⁴ Fig. 2 displays the contrasts in the distinct synthesis procedures and material's structures.

The morphology of Ir- $\text{MnO}_x/\text{N-C}$ is revealed by the transmission electron microscopy (TEM) image shown in Fig. S4.† MnO_x nanoparticles accounted for *ca.* 80 wt% of the hybrid, sizing below 20 nm. They are connected by the contiguous carbon network that offers electron transfer pathways. No Ir or IrO_x nanoparticles are observed. We then examine its structure using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), which is highly sensitive to the variation of atomic weight. The heavier metal element, which scatters the incident electron beams more strongly, shows a brighter intensity. The atomic resolution reveals plenty of sub-nanometric single-atoms that display a much brighter color, but exclusively on the surface of MnO_x in Fig. 3a. The Ir

Fig. 1 The synthetic route to complex 2. (i) 70 °C, 24 h; (ii) Ag_2O , CH_2Cl_2 , 24 h, $(\text{IrCp}^*\text{Cl}_2)_2$.

Fig. 3 (a) HAADF-STEM image of Ir-MnO_x/N-C and the STEM-EDX elemental mapping for (b) the bright-field image, (c) C, (d) Ir and (e) Mn; the scale bar is 20 nm. High resolution HAADF-STEM images of (f) Ir-MnO_x/N-C and (g) C-Ir-MnO_x/N-C, the yellow and white circles indicate Ir atoms on MnO_x and carbon, respectively; the scale bar is 2 nm.

atoms are uniformly dispersed and no clusters are observed (*cf.* the magnified image below). For the elemental mapping at a larger dimension, we analyze the material by energy-dispersive X-ray spectroscopy (EDX). The carbon network indeed spreads over the entire area (70 × 70 nm), connecting each individual MnO_x particle (see Fig. 3b and c). Ir atoms, however, are only observed on the surface of MnO_x (see Fig. 3d and e).

A higher-magnification HAADF-STEM micrograph shown in Fig. 3f confirms that almost all Ir atoms are deposited on MnO_x (circled in yellow). The small portion of Ir found on carbon is ascribed to the interaction between complex 2 and the inherent oxygen-containing groups (OCG) on the surface of carbon (note that the quantity of these OCG is low as reflected by the negligible FTIR signals in Fig. S3†).³⁵ The tiny peak at ~1385 cm⁻¹

was assigned to the in-plane bending vibration of C-O-H. Because of the low density of -OH on carbon compared with that on the metal oxide, our selective adsorption of complex 2 was successfully achieved. In contrast, the control experiment shows that the Ir species in C-Ir-MnO_x/N-C are also atomically dispersed but in this sample they are present on both N-C and MnO_x (Fig. 3g). This structural difference translates to distinct electrochemical performance in the OER (*vide infra*).

Fig. 4a demonstrates the XRD pattern of Ir-MnO_x/N-C. It is clear that MnO is the main phase in the hybrid after forming site-isolated Ir atoms, and the rest of the signals are attributed to either MnO₂ or Mn₃O₄. The apparent peak broadening implies nano-sized MnO_x (*cf.* TEM results above). A calculation *via* the Scherrer equation indicates that the mean size of the crystalline domain is 14.1 nm. Such a nano-structured support possesses high surface area and often the defect density is high too, which is beneficial for a high-loading, yet stable dispersion of Ir.^{27,36,37} No IrO_x or Ir metal peaks were identified in the pattern, suggesting the atomic distribution of Ir. Because most Ir atoms were anchored on MnO_x, the microporous structure and specific surface area of Ir-MnO_x/N-C (138 m² g⁻¹) barely changed compared to those of MnO_x/N-C (135 m² g⁻¹).³⁰

Fig. 4b shows the comparison of the Ir 4f core-level spectra, which are obtained by X-ray photoelectron spectroscopy (XPS), of Ir-MnO_x/N-C before and after the pyrolysis. The strong Ir signals confirm the successful grafting of complex 2 on the hybrid nanorod. These Ir species are slightly reduced after forming Ir-MnO_x/N-C by pyrolysis. As the microscopy/XRD analysis precludes the contribution from IrO_x particles, the consistent high-valence state of Ir suggests the formation of an Ir-O-Mn bond. The peaks at the binding energy of 61.9 eV and 63.2 eV are ascribed to Ir⁴⁺ and its hydrated moieties and/or Ir³⁺ at the 4f_{7/2} core-level, respectively (*cf.* the electrochemical measurement below).³⁸ The deconvoluted peak for Ir 4f_{5/2} also agreed with the above-mentioned analysis. In the N 1s spectra of the sample before pyrolysis, the strong graphitic nitrogen (Ng) signal at 400.7 eV can be assigned to the nitrogen of the carbene ligand of complex 2.³⁹ After pyrolysis, the ratio of Ng decreases dramatically, which is explained by the decomposition of the organic ligand during heat treatment. The residual signals of pyridinic nitrogen at 398.8 eV and oxidized carbon at 401.6 eV

Fig. 4 (a) XRD patterns of Ir-MnO_x/N-C, MnO₂ and Mn₃O₄ labeled in yellow. XPS spectra of (b) Ir 4f and (c) N 1s core levels, the top spectra are from MnO_x/N-C after grafting complex 2 but before pyrolysis, and the bottom spectra are from Ir-MnO_x/N-C.

are contributed by the N-C support. In addition, the survey and the high-resolution spectra of the two samples are compared in Fig. S5–S7 in the ESI.†

To evaluate the catalytic properties of the new materials in water oxidation, we performed electrochemical experiments using a standard three-electrode set-up in 0.1 M KOH electrolyte. Fig. 5a shows the comparison of the linear-sweep voltammograms (LSV) of different catalysts at 1600 rpm. Clearly, the selective immobilization of single-site Ir atoms on these MnO_x/N-C hybrid materials boosts the OER performance substantially. At the benchmark of 10 mA cm⁻², the overpotential (η) of Ir-MnO_x/N-C is as low as 250 mV, corresponding to a 200 mV decrease relative to the parent MnO_x/N-C. The much-improved catalytic performance of the new material is also supported by the small charge transfer resistance recorded in the electrochemical impedance spectroscopy when the cell is biased at 1.5 V vs. RHE (see Fig. S8†). Conversely, the material that contains complex 2 after grafting, but before the pyrolysis (indicated in the graph, as-grafted Ir-MnO_x/N-C), performs poorly, even worse than the MnO_x/N-C support. This implies that the anchored Ir complex 2 is not active under the reaction conditions, and the lower performance implies that the grafted complex 2 is partially blocking the active sites. For comparison, we also evaluated the performance of Ir complex 2 on fluorine-doped tin oxide (Ir-FTO). This material shows a higher onset

potential of 1.46 V (vs. RHE) and a lower catalytic current, also indicating that the activity of Ir-MnO_x/N-C is not from the molecular catalyst. These catalysis experiments suggest that the active site in Ir-MnO_x/N-C contains both Ir and MnO_x. The presence of Ir species in Ir-MnO_x/N-C is verified in the cyclic voltammetry (CV, see Fig. S9†). The reversible charging feature at *ca.* $E_{1/2} = 0.75$ V pertains to the Ir³⁺/Ir⁴⁺ couple while the broader peak at higher potential is attributable to the redox couple of Mn.^{9,40} In comparison, MnO_x/N-C does not show the peaks for the Ir³⁺/Ir⁴⁺ redox couple.³⁰

We then used the classic rotating ring-disc electrode (RRDE) set-up comprising a Pt ring and a glass-carbon disc to determine the faradaic efficiency for O₂ formation. The collection efficiency is determined as 34%, close to the 37% reported by the manufacturer. The calculation from the ring and disc currents confirms that a high faradaic efficiency of >94% is obtained when the potential is >1.45 V (see Fig. 5b). The Tafel plots of MnO_x/N-C, C-Ir-MnO_x/N-C and Ir-MnO_x/N-C are compared in Fig. S10.† The Tafel slopes of C-Ir-MnO_x/N-C and Ir-MnO_x/N-C are essentially the same, implying that the OER might take place on similar active sites *via* the same reaction pathways. Importantly, Ir-MnO_x/N-C is not only more active, but also shows excellent OER stability as the LSVs of Ir-MnO_x/N-C recorded before and after 100 CV cycles (1–1.6 V, 10 mV s⁻¹) are essentially identical (Fig. 5c). The nominal mass activity based on the

Fig. 5 (a) LSV of different catalysts with 95% auto-*iR* correction; (b) RRDE voltammograms of Ir-MnO_x/N-C; (c) LSV before (solid line) and after (dash line) 100 CV cycles, post *iR* and capacitance corrections are applied; (d) nominal mass activity based on the loading of Ir at $\eta = 0.25$ V, the inset compares the Ir-leaching percentage after 100 CV cycles; (e) the proposed pathway of Ir leaching from the carbon in C-Ir-MnO_x/N-C.

loading of Ir reaches 3718 A g^{-1} for the fresh Ir-MnO_x/N-C catalyst at $\eta = 250 \text{ mV}$, which hardly decreases after 100 CV cycles (see Fig. 5d). This material thus substantially outperforms all conventional supported noble metal OER catalysts reported to date in terms of mass activity.^{41,42} A detailed performance comparison with other Ir-containing OER catalysts under both alkaline and acidic conditions can be found in Table S2.† It can be noted that the Ir-MnO_x/N-C catalyst shows the lowest overpotential while demonstrating the highest mass activity at the benchmark of 10 mA cm^{-2} . Besides, chronoamperometry was also performed to evaluate the long-term stability of the catalyst (see Fig. S11†). Being biased at 1.5 V vs. RHE, the electrode hardly shows a current drop over a 40 h test. We then examined the morphology of the used catalyst using TEM. The HAADF image in Fig. S11† clearly indicates the presence of Ir atoms on the surface of MnO_x without migrating to carbon or leaching out.

Although the C-Ir-MnO_x/N-C material, in which Ir atoms are randomly distributed, also performs nicely, it exhibits 50 mV higher onset potential and lower mass activity at $\eta = 250 \text{ mV}$ (for comparison see Fig. 5c). In addition, C-Ir-MnO_x/N-C also suffers from a drastic performance loss after 100 CV cycles, which is evidenced by a drop in mass activity at $\eta = 250 \text{ mV}$ to 268 A g^{-1} . Elemental analysis using inductively-coupled plasma atomic emission spectroscopy reveals that nearly 30% of Ir leaches out from C-Ir-MnO_x/N-C whereas only a minor Ir loss occurs in Ir-MnO_x/N-C (see Fig. S12†), which explains the difference in performance degradation between the two electrocatalysts (inset in Fig. 5d). Apparently, the Ir atoms deposited on the carbon material in C-Ir-MnO_x/N-C are not as firmly bound as those forming Ir-O-Mn under catalytic conditions. At sufficiently high anodic potentials, the Ir catalyzed oxidation may induce the degradation of the surrounding carbons and eventually result in the leaching of the noble metal (see the reaction below). Such scenarios have been observed in several carbon-supported noble metal electrocatalysts.^{43,44} Consequently, the loss of Ir species decreases OER activity. This process is depicted in Fig. 5e.

To get further insight into why this new material shows this excellent performance in water oxidation catalysis, computational studies using density functional theory (DFT) were performed. We selected the rutile MnO₂ (110) surface as the active phase as it shows high stability under OER conditions.⁴⁵ We constructed a coordinatively unsaturated site (*cus*) to accommodate a single Ir atom, denoted as Ir(*cus*)-MnO₂ (Fig. 6). The elementary reaction steps of the proposed OER mechanism under alkaline conditions are shown below. They are modified from those proposed by Rossmeisl and co-workers:⁴⁶

The calculated reaction free-energies and the corresponding overpotentials for MnO₂, Ir(*cus*)-MnO₂ and IrO₂ are shown in Table 1 (also see Fig. 6 and ESI†). The calculated overpotential for MnO₂ is 0.69 V, with the activation of *O to *OOH being the potential-limiting step, in agreement with previous results.⁴⁶ When Ir is incorporated into the MnO₂ lattice in a *cus* position, it results in a reduction in the calculated overpotential of 0.49 V compared to that of MnO₂ (110). Here, the Ir(*cus*) is the active site for the OER, and while the potential-limiting step is still (4) in this case, the *OOH intermediate is more stabilized on the Ir(*cus*) site. The overpotential computed for Ir(*cus*)-MnO₂ is 0.05

Table 1 The calculated free energies and the corresponding overpotentials of various structures used in this study

Material	ΔG_1 (eV)	ΔG_2 (eV)	ΔG_3 (eV)	ΔG_4 (eV)	η_{OER} (V)
MnO ₂ (110)	1.82	1.18	1.92	0.00	0.69
Ir(<i>cus</i>)-MnO ₂	0.71	1.34	1.72	1.15	0.49
IrO ₂ (110)	0.31	1.26	1.77	1.58	0.54

Fig. 6 Structures of (a) rutile MnO₂, (b) Ir(*cus*)-MnO₂, and (c) IrO₂; (d) volcano-activity plot for various structures used in this study. Open circles indicate calculated values of the overpotential.

V lower than that of the state-of-the-art $\text{IrO}_2(110)$ catalyst. Other configurations of the Ir single atom on different phases/orientations of MnO_x should be further examined using both experimental and computational approaches, which can deepen the understanding of the exact nature of the active site during OER catalysis.

3. Conclusion

Water oxidation catalysis at a sufficient rate and low overpotential is of crucial importance for the generation of sustainable fuels. We report a new strategy that provides hybrid materials with superior properties in electrocatalytic water oxidation. A stable Ir precursor complex utilized with a trimethoxysilane linker offers a highly selective method to uniformly deposit site-isolated Ir atoms on the metal-oxide surface of a $\text{MnO}_x/\text{N-C}$ hybrid. The obtained composite material shows water oxidation catalysis at 10 mA cm^{-2} , with an overpotential as low as 250 mV, and excellent stability. DFT calculations show that the origin of the catalyst performance might be the presence of isolated Ir species. This shows the potential of this new approach, which opens up new opportunities for the design of other hybrid materials for energy and catalysis applications.

Conflicts of interest

There are no conflicts to declare.

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References

- 1 N. S. Lewis and D. G. Nocera, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 15729–15735.
- 2 B. Dunn, H. Kamath and J. M. Tarascon, *Science*, 2011, **334**, 928–935.
- 3 F. Bonaccorso, L. Colombo, G. H. Yu, M. Stoller, V. Tozzini, A. C. Ferrari, R. S. Ruoff and V. Pellegrini, *Science*, 2015, **347**, 1246501.
- 4 B. Y. Guan, X. Y. Yu, H. B. Wu and X. W. Lou, *Adv. Mater.*, 2017, **29**, 1605902.
- 5 W. Ng, Y. Yang, K. van der Veen, G. Rothenberg and N. Yan, *Carbon*, 2018, **129**, 293–300.
- 6 S. Dunn, *Int. J. Hydrogen Energy*, 2002, **27**, 235–264.
- 7 J. M. Thomsen, S. W. Sheehan, S. M. Hashmi, J. Campos, U. Hintermair, R. H. Crabtree and G. W. Brudvig, *J. Am. Chem. Soc.*, 2014, **136**, 13826–13834.
- 8 X. X. Zou and Y. Zhang, *Chem. Soc. Rev.*, 2015, **44**, 5148–5180.
- 9 S. W. Sheehan, J. M. Thomsen, U. Hintermair, R. H. Crabtree, G. W. Brudvig and C. A. Schmuttenmaer, *Nat. Commun.*, 2015, **6**, 6469.
- 10 W. Liu, L. L. Cao, W. R. Cheng, Y. J. Cao, X. K. Liu, W. Zhang, X. L. Mou, L. L. Jin, X. S. Zheng, W. Che, Q. H. Liu, T. Yao and S. Q. Wei, *Angew. Chem., Int. Ed.*, 2017, **56**, 9312–9317.
- 11 Y. Jiao, Y. Zheng, M. T. Jaroniec and S. Z. Qiao, *Chem. Soc. Rev.*, 2015, **44**, 2060–2086.
- 12 Y. Gorlin and T. F. Jaramillo, *J. Am. Chem. Soc.*, 2010, **132**, 13612–13614.
- 13 J. Masa, W. Xia, I. Sinev, A. Q. Zhao, Z. Y. Sun, S. Grutzke, P. Weide, M. Muhler and W. Schuhmann, *Angew. Chem., Int. Ed.*, 2014, **53**, 8508–8512.
- 14 Y. Guo, Y. T. Xu, B. Zhao, T. Wang, K. Zhang, M. M. F. Yuen, X. Z. Fu, R. Sun and C. P. Wong, *J. Mater. Chem. A*, 2015, **3**, 13653–13661.
- 15 A. Aijaz, J. Masa, C. Rosler, W. Xia, P. Weide, A. J. R. Botz, R. A. Fischer, W. Schuhmann and M. Muhler, *Angew. Chem., Int. Ed.*, 2016, **55**, 4087–4091.
- 16 L. Wang, X. L. Huang and J. M. Xue, *ChemSusChem*, 2016, **9**, 1835–1842.
- 17 S. Dou, L. Tao, J. Huo, S. Y. Wang and L. M. Dai, *Energy Environ. Sci.*, 2016, **9**, 1320–1326.
- 18 L. J. Dai, M. Liu, Y. Song, J. J. Liu and F. Wang, *Nano Energy*, 2016, **27**, 185–195.
- 19 X. Zhang, R. R. Liu, Y. P. Zang, G. Q. Liu, G. Z. Wang, Y. X. Zhang, H. M. Zhang and H. J. Zhao, *Chem. Commun.*, 2016, **52**, 5946–5949.
- 20 S. Liang, C. Hao and Y. Shi, *ChemCatChem*, 2015, **7**, 2559–2567.
- 21 J. Y. Liu, *ACS Catal.*, 2017, **7**, 34–59.
- 22 C. Zhu, S. Fu, Q. Shi, D. Du and Y. Lin, *Angew. Chem., Int. Ed.*, 2017, **56**, 13944–13960.
- 23 W. K. Xiang, Y. H. Zhao, Z. Jiang, X. P. Li, H. Zhang, Y. Sun, Z. J. Ning, F. P. Du, P. Gao, J. Qian, K. Kato, M. Yamauchi and Y. H. Sun, *J. Mater. Chem. A*, 2018, **6**, 23366–23377.
- 24 J. W. Su, R. X. Ge, Y. Dong, F. Hao and L. Chen, *J. Mater. Chem. A*, 2018, **6**, 14025–14042.
- 25 Y. Chen, Z. Huang, Z. Ma, J. Chen and X. Tang, *Catal. Sci. Technol.*, 2017, **7**, 4250–4258.
- 26 J. Jones, H. Xiong, A. T. DeLaRiva, E. J. Peterson, H. Pham, S. R. Challa, G. Qi, S. Oh, M. H. Wiebenga, X. I. Pereira Hernández, Y. Wang and A. K. Datye, *Science*, 2016, **353**, 150–154.
- 27 B. Qiao, A. Wang, X. Yang, L. F. Allard, Z. Jiang, Y. Cui, J. Liu, J. Li and T. Zhang, *Nat. Chem.*, 2011, **3**, 634.
- 28 S. F. J. Hackett, R. M. Brydson, M. H. Gass, I. Harvey, A. D. Newman, K. Wilson and A. F. Lee, *Angew. Chem., Int. Ed.*, 2007, **46**, 8593–8596.
- 29 B. Hua, Y.-F. Sun, M. Li, N. Yan, J. Chen, Y.-Q. Zhang, Y. Zeng, B. Shalchi Amirkhiz and J.-L. Luo, *Chem. Mater.*, 2017, **29**, 6228–6237.

- 30 J. Pandey, B. Hua, W. Ng, Y. Yang, K. van der Veen, J. Chen, N. J. Geels, J.-L. Luo, G. Rothenberg and N. Yan, *Green Chem.*, 2017, **19**, 2793–2797.
- 31 D. G. H. Hetterscheid and J. N. H. Reek, *Chem. Commun.*, 2011, **47**, 2712–2714.
- 32 J. M. Koelewijn, M. Lutz, W. I. Dzik, R. J. Detz and J. N. H. Reek, *ACS Catal.*, 2016, **6**, 3418–3427.
- 33 J. M. Koelewijn, M. Lutz, R. J. Detz and J. N. H. Reek, *ChemPlusChem*, 2016, **81**, 1098–1106.
- 34 J. Lin, A. Wang, B. Qiao, X. Liu, X. Yang, X. Wang, J. Liang, J. Li, J. Liu and T. Zhang, *J. Am. Chem. Soc.*, 2013, **135**, 15314–15317.
- 35 M. L. Studebaker, E. W. D. Huffman, A. C. Wolfe and L. G. Nabors, *Ind. Eng. Chem.*, 1956, **48**, 162–166.
- 36 P. Hu, Z. Huang, Z. Amghouz, M. Makkee, F. Xu, F. Kapteijn, A. Dikhtiarenko, Y. Chen, X. Gu and X. Tang, *Angew. Chem., Int. Ed.*, 2014, **53**, 3418–3421.
- 37 F. Dvořák, M. Farnesi Camellone, A. Tovt, N.-D. Tran, F. R. Negreiros, M. Vorokhta, T. Skála, I. Matolínová, J. Mysliveček, V. Matolín and S. Fabris, *Nat. Commun.*, 2016, **7**, 10801.
- 38 S. J. Freakley, J. Ruiz-Esquius and D. J. Morgan, *Surf. Interface Anal.*, 2017, **49**, 794–799.
- 39 D. Eisenberg, W. Stroek, N. J. Geels, C. S. Sandu, A. Heller, N. Yan and G. Rothenberg, *Chem.–Eur. J.*, 2016, **22**, 501–505.
- 40 T. Nakagawa, C. A. Beasley and R. W. Murray, *J. Phys. Chem. C*, 2009, **113**, 12958–12961.
- 41 E. A. Paoli, F. Masini, R. Frydendal, D. Deiana, C. Schlaup, M. Malizia, T. W. Hansen, S. Horch, I. E. L. Stephens and I. Chorkendorff, *Chem. Sci.*, 2015, **6**, 190–196.
- 42 E. S. Gnanakumar, W. Ng, F. B. Coşkun, G. Rothenberg, S. Wang, H. Xu, L. Pastor-Pérez, M. M. Pastor-Blas, A. Sepúlveda-Escribano, N. Yan and N. R. Shiju, *ChemCatChem*, 2017, **9**, 4159–4163.
- 43 T. Reier, M. Oezaslan and P. Strasser, *ACS Catal.*, 2012, **2**, 1765–1772.
- 44 W. Wang, J. Luo and S. Chen, *Chem. Commun.*, 2017, **53**, 11556–11559.
- 45 H.-Y. Su, Y. Gorlin, I. C. Man, F. Calle-Vallejo, J. K. Nørskov, T. F. Jaramillo and J. Rossmeisl, *Phys. Chem. Chem. Phys.*, 2012, **14**, 14010–14022.
- 46 I. C. Man, H.-Y. Su, F. Calle-Vallejo, H. A. Hansen, J. I. Martínez, N. G. Inoglu, J. Kitchin, T. F. Jaramillo, J. K. Nørskov and J. Rossmeisl, *ChemCatChem*, 2011, **3**, 1159–1165.