View Article Online View Journal

Journal of Materials Chemistry A

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: W. LUO, W. Xie, M. Li, J. Zhang and A. Züttel, *J. Mater. Chem. A*, 2019, DOI: 10.1039/C8TA11645H.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/materials-a

Journal of Materials Chemistry A Accepted Manuscript

A highly porous indium electrode was prepared with a facile electrodeposition method, which delivers remarkable activity and selectivity towards electroreduction of $\rm CO_2$.



338x190mm (150 x 150 DPI)

Journal Name

ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/



Wen Luo,^{a,b*} Wei Xie,^c Mo Li,^{a,b} Jie Zhang,^{a,b} Andreas Züttel^{a,b}

The electrochemical reduction of CO_2 requires highly active, selective as well as stable electrocatalysts. Herein, we report a three-dimensional hierarchical porous indium catalyst for the electroreduction of CO_2 to formate. In aqueous bicarbonate solution, the catalyst exhibits a high faradaic efficiency for formate (~ 90%) in the potential range of -1.0 to -1.2 V (vs. reversible hydrogen electrode) and reaches an unprecedented formate production rate of 1.14 mmol cm⁻² h⁻¹ at -1.2 V. Additionally, the catalyst also displays a long-term stability (24 h). Density functional theory calculations reveal the catalytically selective nature of In for formate production. Independent of the crystal facet, In surfaces stabilise *OCHO, a key intermediate for the formate pathway, much more effectively than the *H (for the H₂ pathway) and *COOH (for the CO pathway) intermediates. Experimental results demonstrate that the improved CO₂ reduction selectivity on the porous In catalyst originates from the reduced evolution of H₂, which is induced by the high local pH in the vicinity of the electrode. Furthermore, the porous In can also serve as a template to synthesise a porous Pd–In catalyst for tuning the selectivity of formate and CO, demonstrating its promising potential for CO₂ electroreduction.

1. Introduction

Electrochemical reduction of carbon dioxide (CO₂RR) into useful chemicals and carbon-based fuels using renewable sources of electricity is a promising strategy to reduce CO₂ emissions by replacing existing petrochemical-based processes. Among CO₂RR products, formic acid (or formate) is an attractive chemical that has been widely used in cleaning products, for feed preservation, and in the leather processing industry.1 Additionally, the electrochemical formate production process can also be integrated with biological formate conversion process to generate higher alcohols.^{2,3} However, despite that the equilibrium potential for this 2-proton/electron reaction $(CO_2 \rightarrow HCOOH)$ at pH 7 is approximately 0 V (compared to a reversible hydrogen electrode, RHE; all potentials in this paper are versus RHE unless otherwise specified), at low overpotentials the reaction efficiency is limited by sluggish kinetics. Moreover, the poor selectivity due to the myriad possible reaction pathways for CO2RR and, in particular, the competitive hydrogen evolution reaction (HER) also represents a significant challenge for this reaction. Therefore, it is highly



Early studies have identified several transition and posttransition metals, including Cd, Hg, In, Sn, Tl, Pb, and Bi, as selective catalysts for CO2-to-formate.4,5 Among them, In is suggested as a potential catalyst for practical formate production, since it is less toxic and more environmentally benign than many of its neighbours.^{2–6} Recent researches have shown that In-based catalysts can readily reduce CO₂ to formate in an aqueous electrolyte with faradaic efficiencies (FE) >80%; however, with limited current density at reasonable overpotentials. For example, oxidised In foil and In nanoparticles were found to reduce CO₂ to formate with a selectivity of >90%, but the current densities were lower than 10 mA cm⁻² at the potentials of highest formate FEs.^{7,8} On a dendrite In electrode, the maximum FE (~ 86%) was achieved at -0.86 V with a current density of 5.8 mA cm⁻².9 Even on a gas diffusion In/carbon electrode, the total current density only reached 6.2 mA cm⁻² at -1.2 V.¹⁰ Moreover, the stability of Inbased catalysts has not yet been extensively evaluated and no catalyst with more than 2 h stability has been reported.^{9,11} Thus, the performance of In-based catalysts, in terms of selectivity, activity and stability, needs to be greatly improved before any practical applications.

Manipulating the structure of the electrode, particularly creating a highly porous structure, has been recently recognized as an effective means to enhance the catalytic performance. While porous metal electrodes, such as Cu,¹² Ag,¹³ and Au¹⁴ have been fabricated and demonstrated as promising CO_2RR catalysts, a porous In electrode may also be designed. Nevertheless, the special physical and chemical properties of In,



^{a.} Laboratory of Materials for Renewable Energy (LMER), Institute of Chemical Sciences and Engineering (ISIC), Basic Science Faculty (SB), École Polytechnique Fédérale de Lausanne (EPFL) Valais/Wallis, Energypolis, Rue de l'Industrie 17, CH-1951 Sion, Switzerland

^{b.} Empa Materials Science & Technology, CH-8600 Dübendorf, Switzerland ^{c.} INAMORI Frontier Research Center, Kyushu University, 744 Motooka, Nishiku,

Fukuoka 819-0395, Japan.

^{*} Corresponding author: wen.luo@epfl.ch

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Published on 30 January 2019. Downloaded by Western Sydney University on 1/31/2019 11:11:25 AM

ARTICLE

for example, its soft nature (Young's modulus is 11 GPa), low melting point (156.5 °C) and easy to oxidise properties, limit the engineering of its nanostructure. Indeed, not only is such a porous In catalyst still lacking, the reaction mechanisms of CO₂to-formate over In-based catalysts are also not clear. For instance, Bocarsly et al. suggested that the oxidised In layer on the surface of an In electrode may be involved in the CO₂RR reaction by forming a metal carbonate species, which is then reduced to formate.^{7,15} In contrast, Shaughnessy et al. found that an In/In₂O₃ composite catalyst produces CO, rather than formate, at a selectivity near 100%.16 Alternatively, for a dendritic In catalyst, the high local CO₂ concentration near the electrode induced by the local electric field was proposed as the reason for the high catalytic performance observed.9,17 The ambiguous CO₂RR mechanism greatly impedes the development of advanced In catalysts; thus, systematic studies using experimental and theoretical methods are urgently required to gain further insights into the reaction mechanisms. In this work, we developed a three-dimensional (3D) hierarchical porous In catalyst (hp-In) for CO₂RR using a facile electrochemical deposition method. Under a high current deposition condition, H₂ bubbles generated from the accompanying HER serve as a geometric template.¹⁸ The asprepared hp-In electrode exhibits a high faradaic efficiency for formate (~90%) and reaches the highest formate production rate (1.14 mmol $cm^{-2} h^{-1}$ at -1.2 V) among the state-of-the-art catalysts in aqueous solution reported. Density functional theory (DFT) calculations combined with detailed experimental studies revealed that the high formate selectivity over hp-In is attributed to the strong adsorption of an *OCHO intermediate on In facets and the high local pH near the highly roughened electrode surface. Furthermore, the hp-In electrode was also applied as a template to synthesise a porous Pd-In catalyst for tuning the CO₂RR selectivity.

2. Experimental part

2.1 Materials. Cu mesh (80 mesh), Ni mesh (100 mesh), In foil (0.127 mm, 99.99% metal basis), $In_2(SO_4)_3$ (99.99% metal basis), $PdCl_2$ (99.9% metal basis), HNO_3 (2.0 N standardised solution) and HNO_3 (65%) were purchased from Alfa Aesar. (NH_4)₂SO₄ (99.5%), H_2SO_4 (75%) and $KHCO_3$ (99.5%) were purchased from Carl Roth. NaCl (99.5%) was purchased from Fluca. HCl (32%) was purchased from Reactolab SA. A Ag/AgCl reference electrode (3 M NaCl) was purchased from ALS Corporation, Japan. High-purity CO₂ (99.999%) and N₂ (99.999%) were supplied by Cabagas, Switzerland. All chemicals were used as received without further purification. Electrolyte solutions were prepared using Milli-Q water (Millipore, 18.2 M Ω cm).

2.2 Sample preparation. The *hp*-In was prepared by an electrochemical deposition method modified from previous reports.^{12,18} The electrodeposition was performed in a two-electrode cell using the Cu mesh as the working electrode (and also providing a substrate for the *hp*-In) and Pt wire as the counter electrode. The Cu mesh ($0.4 \text{ cm} \times 0.5 \text{ cm}$, with a $0.2 \text{ cm} \times 0.5 \text{ cm}$ rectangular tip for holding) was sonicated in

Journal Name

acetone, water, and 2 M HNO₃ for 5 min, sequentially, and then washed with Milli-Q water and dried in a flow of N_{23}^{3} The Work high electrolyte was prepared with a 1.5 M (NH₄)₂SO₄ and 0.03 M In₂(SO₄)₃ aqueous solution. The *hp*-In was deposited on the Cu mesh at a constant current density of 1.0 mA cm⁻² (normalised to the geometric surface area) for 120 s. After the deposition, the as-prepared *hp*-In was carefully washed with Milli-Q water, subsequently dried in a N₂ flow, and then used as an electrode for CO₂RR.

In foil (Figure S1), used as a reference sample, was cleaned sequentially with acetone, water, and 2 M HCl for 5 min and then washed with Milli-Q water and dried in a N_2 flow.

The two additional porous In electrodes used in control experiments were prepared by the same method as that used for *hp*-In but under different conditions: sample 1, 0.125 mA cm⁻² for 500 s (named *hp*-In-0.125) and sample 2, 0.5 mA cm⁻² for 200 s (named *hp*-In-0.5).

Porous In on Ni mesh electrode was prepared using a 1.5 M $(NH_4)_2SO_4$ and 0.03 M $In_2(SO_4)_3$ aqueous solution. In was deposited on Ni mesh at 2.0 A cm⁻² for 180 s.

Porous Pd electrode was prepared using a 2.0 M H_2SO_4 , 2 mM $PdCl_2$ and 50 mM NaCl aqueous solution. Pd was deposited on Cu mesh at 2.0 A cm⁻² for 200 s.¹⁹

Pd–In electrodes were prepared by dipping the fresh hp-In into 1.0 mL PdCl₂ aqueous solutions for 5 min. PdCl₂ solutions with different concentrations (0.1, 0.5, 1.0 and 2.0 mM) were prepared with 0.1 M NaCl and certain amount of PdCl₂. After Pd deposition, the as-prepared electrodes were carefully washed with Milli-Q water and sequentially dried under N₂ flow. The Pd-In electrodes were denoted as Pd-In-0.1, Pd-In-0.5, Pd-In-1.0 and Pd-In-2.0 respectively, according to the concentration of [PdCl₄]²⁻ in the solutions.

2.3 Characterisation. Scanning electron microscopy (SEM) images were taken on an FEI Teneo system and X-ray diffraction (XRD) patterns were obtained from a Bruker D8 Advance equipped with a Cu Ka X-ray source at 40 kV and 40 mA. The X-ray photoelectron spectroscopy (XPS) results were recorded using a Phoibos 100 (SPECS) hemispherical electron analyser with Mg K α X-ray source (hv = 1253.6 eV). The XPS spectra were recorded at a pass-energy of 90 eV for the survey and 20 eV for the narrow scans in the fixed analyser transmission mode. The samples are conductive, and thus no charge compensation was needed. The ICP-OES measurements were taken using an Agilent 5110 inductively coupled plasma optical emission spectrometry (ICP-OES) system. All the samples were dissolved in 65% $HNO_{\rm 3}$ and then diluted with Milli-Q water. Pd and In standard solutions with different concentrations were prepared with PdCl₂ and In₂(SO₄)₃ in 2% HNO₃, respectively. The obtained mass loadings of Pd and In were listed in Table S1.

2.4 Electrochemical measurements. All electrochemical measurements were performed with a two-compartment cell (H-Cell) and the working and counter electrode compartments were separated with a Nafion membrane (212, DuPont). An Autolab PGSTAT 204 potentiostat was used to record the data.

Chemistry A Accepted Manu

ournal of Materials

ARTICLE

A piece of platinum gauze (2.5 cm \times 2.5 cm) and a Ag/AgCl electrode were applied as the counter and reference electrodes, respectively.

The the electrochemical surface area (ECSA) of the electrode was determined by measuring the double-layer capacitance (C_{dl}). Cyclic voltammetry (CV) was performed at scan rates of 0.1, 0.15, 0.2, 0.25, and 0.3 V s⁻¹ in a N₂-bubbled 0.1 M KHCO₃ electrolyte. The potential window of CV was selected to be between -0.34 and -0.44 V, where only double-layer charging and discharging is relevant. The total charging current at a given scan rate was determined as the difference between the anode current and the cathode current at -0.39 V. These capacitive currents were plotted against the scan rate, and the slope of this plot was divided by 2 to obtain the value of C_{dl}. The ECSAs of the porous samples were then calculated using their C_{dl} values divided by 30.5 μ F cm⁻² (the C_{dl} of the In foil, which is very similar to the value of other planar metal surfaces^{20,21}).

Electrochemical CO₂ reduction experiments were conducted with the H-Cell. Each compartment of the cell was filled with 30 mL of 0.1 M KHCO₃ solution with 15 mL left as dead volume. CO₂ was introduced into the cathodic compartment at a flow rate of 21 mL min⁻¹ (controlled by a mass flow controller, (EL-Flow, Bronkhorst)) during the experiments. Prior to the start of each experiment, the catholyte was saturated with CO₂ for at least 30 min (the pH value was measured to be 6.8). To enhance the mass transport of CO₂ during electrolysis, the catholyte was stirred continuously using magnetic agitation. All potentials were recorded against the Ag/AgCl reference electrode and then converted into RHE values using: E (vs. RHE) = E(vs. Ag/AgCl) + 0.21 V + 0.0591 V × pH. The uncompensated ohmic loss (iRu) was corrected in situ via the current interrupt method, and compensation levels were set to 85% of the measured *i*Ru.^{22–26}

The same protocol was used for the stability test; however, in order to avoid the accumulation of formate in the catholyte, a multi-channel peristaltic pump (ISMATEC, REGLO Digital MS-4/8 834) was used to exchange the catholyte. That is, fresh CO_2 -saturated 0.1 M KHCO₃ was pumped into the cathode compartment at a speed of 23 mL min⁻¹ while, concurrently, the catholyte was also pumped out and collected at the same flow rate to maintain a constant level of catholyte (30 mL) in the cathode compartment.

2.5 Product distribution analysis. The gas-phase products were detected online with a gas chromatograph (GC, SRI instruments 8610C) equipped with a thermal conductivity detector (TCD) and a flame ionisation detector (FID, with a methaniser). The CO_2 gas flow, together with the products from the cathodic compartment, was vented directly into the sampling loop of the GC. Aliquots were collected every 20 min during the reaction, and at least three injections were measured for each experiment. Liquid products were collected after the reaction and were detected by high-performance liquid chromatography (HPLC, Thermo Scientific, Dionex UltiMate 3000 Standard System).²⁷

2.6 DFT models and calculations. All plane-wave DFT calculations were carried out with the Vienna ab initio Simulation Program (VASP)²⁸ using the generalised gradient

approximation (GGA) and Perdew, Burke, and Ernzerbof ($(BEE)_{Pe}^{2Pe}$ exchange-correlation function. Four In surfaces, including (101), (002), (110), and (112), were modelled using three-layer (2 × 2) periodic unit cells, with the bottom layer fixed during optimisation while the remaining atoms relaxed. Projector augmented wave pseudopotentials³⁰ were used to describe the interactions between the ions and the electrons in expanding plane waves with a cutoff energy of 400 eV and a (5,5,1) k-point sampling Monkhorst-Pack grid.³¹ Different adsorption configurations with the lowest energy were used for the final free energy diagrams.

All thermodynamic properties were calculated based on the molecular vibration analysis from the DFT calculations. The Gibbs free energies were calculated at 298 K and 1 atm. according to G = $E_{DFT}+E_{ZPE}+\int_{0}^{298}\!C_VdT-TS$, where E_{DFT} is the DFT total energy, $\mathrm{E}_{\mathrm{ZPE}}$ is the zero-point vibrational energy (ZPE) obtained from the calculated vibrational frequencies, the thermal capacity $\int_0^{298} C_V dT$ was calculated from the heat capacity, T is the temperature, and S the entropy of the studied system. For the gas molecules, including H₂, CO₂, CO, H₂O, and HCOOH, the ideal gas approximation was used, and for the adsorbates, the harmonic approximation was used. Corrections for CO₂, CO, and HCOOH were applied using the values for the PBE function to describe accurately the free energy of the reaction for CO₂RR.³² An approximate solvation correction to account for the effect of water was applied for *COOH (stabilised by 0.25 eV). Free energy diagrams were generated using the CHE method.33 Additional details of the DFT calculations are provided in the Supporting Information.

3. Results and discussions

3.1 Synthesis and characterizations of hp-In.

The hp-In catalyst was synthesised by a facile one-step template-free electrodeposition method at a constant current density of -1.0 A cm⁻² for 120 s (Figure 1a and Figure S2). The concomitant hydrogen bubbles generated during the electrodeposition served as a geometric template, accounting for the formation of hierarchical porous structures. (NH₄)₂SO₄ was used as solvent to facilitate H₂ evolution over the initial deposited In layer, since In has a high hydrogen overpotential.⁴ A copper mesh was selected as a support rather than a foil, as it allows the transport of electrolyte around the mesh to compensate the concentration gradient caused by electrodeposition, and therefore ensures the uniform growth of porous In. As revealed by the SEM images (Figure 1c-e), the In layer was deposited homogeneously on the support with uniformly interconnected macropores (~150 µm, Figure 1c) which were inherited from the Cu mesh (Figure 1b). Close observation revealed that densely packed In 'leaves' were formed uniformly and vertically on the Cu wire, and between the leaves, smaller macropores with diameters of 10 to 30 μ m were observed (Figure 1c-e). In addition, each of the In leaves was fully covered by

This journal is C The Royal Society of Chemistry 20xx

Published on 30 January 2019. Downloaded by Western Sydney University on 1/31/2019 11:11:25 AM

ARTICLE

Journal Name

View Article Online DOI: 10.1039/C8TA11645H



Figure 1 (a) Schematic illustration for the synthesis of hp-In. (b) SEM image of Cu mesh. (c)-(e) SEM images of hp-In at different magnifications. (f) XRD patterns of In foil and hp-In. (g) XPS In 3d spectra of In foil and hp-In.

interconnected micro-gullies of appropriately 1 μ m width (Figure 1e). These morphological features clearly demonstrate the successful electrodeposition of *hp*-In onto the Cu mesh with a structure consisting of three sizes of progressively larger pores.

The crystal structure of the *hp*-In catalyst was examined by XRD. As shown in Figure 1f, diffraction peaks located at approximately 32.7°, 36.1°, 38.9°, 54.2°, 56.3°, 63.0°, 66.8°, and 68.9° were consistent with those of the In foil and the metallic In phase (JCPDS card No. 01-80-5354). Additional peaks were observed at 43.3° and 50.4° on the hp-In pattern, arising from the Cu mesh support. The sharp diffraction peaks of the hp-In indicate the high crystallinity of the deposited In (the average crystallite size calculated using the Scherrer equation with full profile fitting was ~60 nm). XPS was performed to investigate the surface chemical composition and oxidation state of the hp-In. No spectrum from Cu was observed in the survey spectrum (Figure S3), implying that the Cu mesh was fully covered by the porous In layer. Specifically, the In $3d_{5/2}$ XP spectra of the hp-In and In foil were deconvolved into two peaks (Figure 1g), which were attributable to the metallic In (443.9 eV) and In₂O₃ (445.1 eV). The partially oxidised In could be removed by Ar⁺ sputtering performed in the XPS chamber (Figure S4), therefore the oxidation of In should be associated with oxidation in air prior to the XPS measurement. Such a thin layer of oxidised In could be readily reduced at the beginning of CO₂RR.⁷

3.2 CO₂RR performance over In foil and hp-In.

The electrochemical performance of the hp-In was initially investigated by CV measurements in 0.1 M KHCO₃ saturated with N₂ or CO₂ (Figure 2a and Figure S5). The In foil was also tested under identical conditions for the purpose of comparison. As shown in Figure 2a, in all cases, oxidation peaks appeared at ca. -0.1 V, corresponding to the oxidation of In⁰ to In^{3+.7,9,16} The reduction peaks appeared at around -0.4 V, with peak areas similar to the oxidation peaks, which corresponds to the reduction of In³⁺ to In^{0,7,9,16} Interestingly, the inset in Figure 2(a) shows that the redox peaks of In foil obtained in CO₂ are lower than those obtained in N_2 , which could be due to the presence of adsorbed species during CO₂RR.³⁴ While in case of hp-In, the redox peaks are much larger compared with those of In foil, thus no obvious influence from reaction intermediates is observed. At more negative potentials (< -0.6 V), the increase in current densities (geometric current density, unless otherwise specified) under N₂ conditions could be attributed to the HER, while under CO₂ conditions it is due to the HER and CO₂RR. Obviously, both the In foil and hp-In electrodes show higher current densities in CO_2 conditions than those in N_2 , demonstrating the active nature of In in reducing CO₂ rather than H₂O. Moreover, due to its porous structure, hp-In exhibits much higher current density than that of In foil.

To identify and quantify the reduction products, bulk electrolysis was conducted in CO_2 -saturated 0.1 M KHCO₃. The FEs of the reduction products in the potential range of -0.6 to -1.2 V are displayed in Figure 2b-c for In foil and *hp*-In, respectively. As shown, only H₂, CO, and formate were detected as the reduction products from the two electrodes, with a total

Journal Name

FE of approximately 100%. Figure 2b shows that formate and H₂ are the main products obtained from the In foil electrode, the FEs of which are strongly dependent on the applied potential, whereas the FE for CO is limited to less than 13% over the entire potential range. Note that trace amounts of H₂, CO, and formate can also be detected at -0.6 and -0.7 V, but are hardly quantified because of the limits of detection. From -0.8 V, formate starts to be reliably and reproducibly detected with an FE of 29.9%, while H_2 exhibits an FE of 51.3%. With the decrease in the applied potential, the formate selectivity increases dramatically to 64.9% at -1.0 V and reaches a plateau of ca. 70% at -1.2 V. Conversely, the FE for H₂ decreases gradually to 12.2%. This product distribution agrees well with that observed on other In-based electrodes, where formate is the dominant product reduced from CO₂, while H₂ is the competitive product from the HER.^{7,9} Surprisingly, on the *hp*-In electrode, the FE for H₂ is significantly suppressed to less than 10% in the entire potential range, and CO₂ is reduced to formate and CO with FEs of >90% (Figure 2c). Formate is initially detected at -0.6 V with an FE of 61.2%, which gradually increases to 88.2% at -1.0 V and is then maintained at ~90% until -1.2 V. In concert with the rise of formate FE, the CO FE declines from 29.4% to 2.4% as the applied potential shifts negatively from -0.6 V to -1.2 V. To futher confirm that the Cu mesh dese not play a catalytic role during CO₂RR, we prepared a porous In electrode supported on a Ni mesh and evaluated its CO₂RR performance. While bulk Ni is known to be inactive for $\rm CO_2 RR,^4$ the product distribution of porous In on Ni mesh is similar as that of hp-In (Figure S6). This indicates that the metal meshes only serve as support and current collector, and it also demonstrates the universality of our method in preparing supported porous In catalysts.

The total current density of the In foil and the *hp*-In are also plotted against the working potential (Figure 2d). Consistent with the CV results (Figure 2a), *hp*-In shows significantly higher current densities than In foil. With an increase in the overpotential, the total current on the *hp*-In reaches a remarkably high value of 67.5 mA cm⁻² at –1.2 V. This improved current density on *hp*-In may be attributable to its enlarged surface area. To confirm this, ECSA was calculated from the double-layer capacitance derived from the CV data (Figure S7 and Table S2). The results reveal that *hp*-In exhibits a 27.6-fold higher ECSA than In foil due to its highly porous structure. Taken together, these results demonstrate that by creating a 3D porous structure, the CO₂RR performance of the Invelectrodenin terms of both current density and formatel:selectivity/telf4be dramatically improved.

Because of the outstanding current densities and the high formate FEs, the *h*p-In electrode also delivers superior formate production rates (FPRs). As shown in Figure 2e, the FPRs of *hp*-In are plotted against the applied potential and compared with those of other state-of-the-art formate-producing catalysts, including In, Sn, Bi, and Pb etc. At more positive potentials (-0.6 to -1.0 V), the FPRs of the *h*p-In electrode are among the highest values delivered by the most active formate-producing catalysts under optimised conditions. As the FPR of the *h*p-In increases monotonically with the overpotential, it reaches an unprecedented value of 1.14 mmol cm⁻² h⁻¹ at -1.2 V.

The durability of a catalyst is essential for practical applications; however, the stability of In-based catalysts has not yet been extensively evaluated and no catalysts with more than 2 h stability have been reported.9,11 Therefore we examined the long-term performance of the hp-In electrode in 0.1 M KHCO₃ at -1.0 V. According to previous results,35 the accumulation of formate in the cathodic compartment of the H-Cell can lead to a decrease of the formate FE, as also observed in our initial tests (Figure S8). To isolate the influence of the formate accumulation, we exchanged the electrolyte in the cathodic compartment with fresh CO2-saturated 0.1 M KHCO3 at a constant flow rate (23 mL h⁻¹) using a peristaltic pump. As shown in Figure 2f, the current density was maintained at around 33 mA during the 24 h stability test, with no apparent signs of activity loss. The formate FE showed an initial decay from ~90% to ~78% over the first 9 h, and then stabilised at ~76%. Notably, the decrease in the formate FE was compensated by the CO FE, which increased from ~6% to ~16%, while the FE for H_2 remained at a low level (<10%). We speculate that the increase in CO selectivity in the first few hours is due to the access of the electrolyte/gas bubbles at the interface of the In layer and the Cu mesh, as the Cu-In interface has been suggested to be highly selective for CO₂-to-CO.³⁶ The morphology of the sample after the stability test had not changed and the porous 3D structure was well preserved, as revealed by the SEM results (Figure S9). Taken together, the high current density, along with the high formate selectivity and long-term stability, demonstrates the significant potential of hp-In for CO₂RR applications

ARTICIF

Journal Name



Figure 2 (a) Cyclic voltammograms of the In foil and hp-In in N₂- and CO₂-saturated 0.1 M KHCO₃ at a scan rate of 50 mV/s; note that magnetic stirring and ohmic loss compensation were not applied during CV scans to avoid a noisy background, which leads to lower total current densities compared with the values shown in (d). (b) Potential dependent faradaic efficiencies for In foil and (c) hp-In. (d) Comparison of current densities for In foil and hp-In obtained at various applied potentials. (e) Formate production rate at various applied potentials on the hp-In electrode, along with an overview of the formate production rate on the state-of-the-art CO₂-to-formate catalysts. The catalysts were classified as: In (red),⁶⁻⁹ Sn (dark-blue),³⁷⁻⁴⁴ Bi (yellow),^{1,26,45-48} Pb (blue),^{49,50} alloys (black),^{51,52} and non-metal electrodes (magenta).⁵³⁻⁵⁵ The details are summarised in Figure S10 and Table S3 in the Supporting Information. (f) Catalytic stability performance for hp-In.

3.3 Mechanism of CO₂RR to formate on In facets.

Calculations using DFT have become a powerful tool for studying the reaction mechanisms of CO₂RR on model catalysts. Computational investigations on metals such as Cu,^{32,56} Au,^{17,57} Pd⁵⁸ and Zn⁵⁹ have provided mechanistic insights into the reaction pathways and predicted appropriate structures for advanced catalysts. However, no DFT simulation has been conducted for In-based catalysts for CO₂RR. Therefore, to reveal the origin of the preferential selectivity towards formate over In-based catalysts, we calculated the adsorption energies of the key reaction intermediates over various In facets. During the DFT calculation, HCOOH was considered to be a reduction product rather than formate, since decoupling the proton and electron donations remains computationally unviable.^{32,60} According to the experimental results, HCOOH and CO are the only products reduced from CO₂ over the In electrodes, both of which involve two proton-coupled-electron-transfer (PCET) processes. Theoretical and experimental studies have suggested that CO₂-to-HCOOH proceeds through formate intermediate (*OCHO) and CO2-to-CO proceeds through carboxyl intermediate (*COOH),1,32,60-62 as shown in the following equations (eqs. 3-4):

$$CO_2 + H^+ + e^- + * \rightarrow *OCHO$$
(1)

*OCHO + H⁺ + e⁻
$$\rightarrow$$
 HCOOH (2)

$$CO_2 + H^+ + e^- + * \rightarrow *COOH$$
(3)
*COOH + H⁺ + e⁻ $\rightarrow CO$ (4)

*COOH + H⁺ + e⁻
$$\rightarrow$$
 CO

HER as a competitive reaction of CO₂RR proceeds via the *H intermediate (eqs 5, 6 or 5, 7):

H⁺ + e⁻ + * → *H	(5)
[*] H + H ⁺ + e ⁻ → H ₂ , or	(6)
$*H + *H \rightarrow H_2$	(7)

In all of these equations, the asterisk (*) indicates an active catalytic site. It is generally believed that the selectivity of these three products is determined primarily by the relative stability of their reaction intermediates. Therefore, we calculated here the free energy changes for the first PCET process.63,64 We considered four different In facets, including (101), (002), (110) and (112). The (101) facet was chosen because it is the predominantly exposed crystal plane, as observed in the XRD results; moreover, it is the energetically most stable low-index crystal facet of In. Although the (002), (110), and (112) facets are less prevalent in the XRD patterns, they were chosen to study the influence of crystal facet on the reaction pathways.32,65

Figure 3a presents the clean (101) surface (Figure 3a1) and the stable adsorption geometries of *H (Figure 3a2), *COOH (Figure 3a3) and *OCHO (Figure 3a4) (adsorption structures on other facets can be found in the Supporting Information, Table S4). The computational results suggest that a hollow site is energetically preferred for the adsorption of H*. For the *COOH intermediate, C adsorbs on the In atom with O approaching the neighbouring In atom. In case of the *OCHO intermediate, the results show that its most energetically favourable configuration is the binding of two In atoms via two oxygen atoms, similar to the adsorption structure on Bi and Sn.^{1,66} Based on these optimised adsorption geometries, we calculated Published on 30 January 2019. Downloaded by Western Sydney University on 1/31/2019 11:11:25 AM

ARTICLE



Figure 3 (a) DFT models of (a1) clean (101) surface; (a2) optimised adsorption configuration of *H on (101); (a3) side (top) and top (bottom) views of optimised adsorption configuration of *COOH on (101); and (a4) side (top) and top (bottom) views of optimised adsorption configuration of *OCHO on (101). (b) Free energy diagrams calculated for the HER, CO₂-to-CO, and CO₂-to-HCOOH on (101), (002), (110), and (112).

the Gibbs free energy changes (Δ G) at U = 0 V potential using the computational hydrogen electrode (CHE) model for the CO₂RR and HER processes (Figure 3b).³² For the HER, the formation of *H on all the four In facets is significantly uphill in energy (0.80–0.93 eV), indicating that a high overpotential is needed for the evolution of H₂. For the CO₂RR pathways, adsorption intermediate on In surfaces, whether the surface is planar (e.g. (101)) or stepped (e.g. (112)). Thus, the readily adsorbed *OCHO would occupy the active sites and inhibit the adsorption of *H and *COOH, leading to a high HCOOH selectivity. Moreover, the total reaction overpotential is estimated to be >0.4 V, which agrees reasonably well with our experimental finding (~0.55 V).

Although all the studied surfaces show similar free energy diagrams for the specified product, facet-dependent adsorption energy differences can still be observed. For example, compared to other facets, the low index (101) surface stabilises the *OCHO intermediate most effectively but stabilises *H and *COOH more difficultly, thus is suggested to be highly selective towards HCOOH, even though a high overpotential is required (0.70 V). In contrast, the stepped (112) surface is more favourable in stabilising *H and *COOH relative to the other facets, suggesting that relatively low overpotentials are required for the H₂ (0.8 V) and CO (0.38 V) pathways. The other two facets, (002) and (110), are proposed to be the most promising surfaces for the production of HCOOH, since they have low ΔG for the *OCHO \rightarrow HCOOH step but relatively high ΔG for *H and *COOH adsorption steps. Therefore, we can predict that at low overpotentials, open facets such as (002) and (110) are more active towards HCOOH, while at high overpotentials (101) may play a dominant role in the production of HCOOH. Together, by comparing the three reaction pathways on different In facets, we demonstrate that, from a thermodynamic point of view, In is intrinsically selective for CO₂RR towards formate due to the preferred adsorption of the

*OCHO intermediate rather than *H and *COOH, which rationalises the experimentally observed high formate selectivity over In-based catalysts.^{6,9}

3.4 Origin of the improved CO₂RR selectivity over hp-In.

While DFT calculations provide reasonable interpretations of the preferential production of formate over In-based catalysts, further insights into the enhanced CO₂RR selectivity on hp-In are still required. As CO₂RR is performed in an aqueous environment, the improved CO₂RR selectivity can be attributed to the increase of CO₂ reduction activity and/or the decrease of HER activity.^{14,67} To clarify that, we tried to compare the intrinsic activity for formate, CO, and H₂ production for our In electrodes. Besides hp-In and In foil, we prepared two additional lower-porosity In electrodes for better comparison (denoted as hp-In-0.125 and hp-In-0.5 since they were deposited at 0.125 and 0.5 A cm⁻², respectively. Details can be found in the experimental section, Figure 4a, and Figure S11-S13). Specific current densities were calculated by normalising the partial currents of formate, CO, and H₂ to the ECSA of each electrode (Figure 4a). Figure 4b shows that at a low overpotential range (-0.6 to -0.9 V), the four electrodes exhibit identical specific formate current densities $(j_{(HCOO)}, j_{ECSA})$. At high overpotentials (>-0.95 V), the In foil catalyst performs better because mass transfer is limiting the supply of CO₂ to the highly roughened hp-In electrode. Interestingly, the specific CO current densities (j_{(CO)/ECSA}) in Figure 4c follow a very similar trend to that of specific $j_{(HCOO)^{-}/ECSA}$. In stark contrast, the H₂ evolution curves change dramatically. As shown in Figure 4d, over the entire potential range, the higher the ECSA, the lower the specific H₂ current densities $(j_{(H_2)/ECSA})$ observed. These data imply that while the In foil and the hp-In electrodes exhibit similar intrinsic CO and formate activities, the lower HER activity on hp-In leads to the higher CO₂RR selectivity.

Journal Name

View Article Online DOI: 10.1039/C8TA11645H



Figure 4 SEM images and ECSA for the In foil, hp-In-0.125, hp-In-0.5, and hp-In samples. Scale bar of SEM image for the In foil is 20 μ m, and for the other three samples is 150 μ m. Specific activity for (b) formate, (c) CO, and (d) H₂ for the four electrodes evaluated in CO₂ saturated 0.1 M KHCO₃ electrolyte.



Figure 5 (a) Schematic illustration of local pH effect during CO_2RR . (b) CO_2RR performance of hp-In, evaluated in CO_2 saturated 0.1–0.5 M KHCO₃ at -0.8 V (KCl was added to maintain the K⁺ concentration at 0.5 M).



Figure 6 (a) SEM image of hp-In-1.0 sample and the corresponding elemental mappings of Cu, In, and Pd. (b) Pd/In atomic ratios for the porous Pd-In electrodes, obtained from XPS and ICP-OES measurements. (c) Total current density and faradaic efficiencies of CO, formate and H₂ for hp-In, porous Pd-In, and porous Pd electrodes, evaluated in CO₂ saturated 0.1 M KHCO₃ at -0.7 V.

As the HER activity is strongly correlated to the ECSA of the electrode (Figure 4d), we proposed that the reduced HER activity on a high-surface-area electrode is because of the high local pH near the electrode. As illustrated in Figure 5a, when electrolysing CO₂ in an aqueous solution, the pH rises locally at the electrode/electrolyte interface because of the proton consumption for the cathodic reactions (eqs. (1) - (6)). The highly porous structure of the electrode (i.e. hp-In) and the weak buffer capacity of the electrolyte (i.e. CO_2/HCO_3^{-}) are prone to induce high local pH.^{14,68} Therefore, HER activity is postulated to be lower over the high-surface-area hp-In electrode. On the other hand, if we increase the buffer capacity of the electrolyte, a reduced local pH and consequently an increased HER activity is expected.⁶⁹ To verify that, we increased the HCO_{3}^{-} concentration from 0.1 to 0.5 M and performed the CO₂RR on the *hp*-In electrode. KCl electrolyte, which has no buffering ability, was added to the KHCO3 electrolytes to minimise the influence of K⁺ on the activity and selectivity of CO₂RR by maintaining the total K⁺ concentration at 0.5 M.¹⁷ Figure 5b shows that $j_{(H_2)/ECSA}$ rises monotonically with the crease in HCO₃⁻ concentration, confirming that the higher buffering capacity of the electrolyte promoted the HER activity. This result is further supported by the data obtained in other electrolytes, including KCl and K₂HPO₄, where H₂ selectivity is also positively related to the electrolyte buffering ability (Figure S14). Moreover, Figure 5b shows that the specific activities of formate and CO are almost unchanged as the HCO3concentration increases, indicating that under the current experimental conditions, CO₂RR activity is less sensitive to the local pH compared with HER. These data imply that the improved CO₂RR selectivity on hp-In originates from the reduced H₂ activity, which is induced by the high local pH at the vicinity of the electrode. It is worth to mention that despite various nanostructured catalysts have been applied for CO₂RR, the effect of local pH on the catalytic selectivity is often overlooked. In such circumstance, the influence of other factors, such as crystal orientation, defect or oxidation state of the catalyst, could be overestimated. Therefore, we emphasize that further consideration of local pH effect needs to be taken in the interpretation of the reaction mechanisms, as well as the development of electrode materials and reaction cells.

3.5 Porous Pd–In electrodes for CO₂RR.

With its highly porous morphology, *hp*-In can also serve as a template for synthesising other porous electrodes. Recent works have shown that In-based bimetallic catalysts, e.g. Cu–In and Ag–In, are highly selective for the CO_2RR to $CO_{36,70,71}$ Inspired by that, we deposited Pd onto the *hp*-In electrode *via* a facile galvanic replacement method to fabricate a porous Pd–In electrode for CO_2RR . The catalysts were prepared by dipping the *hp*-In into PdCl₂ solutions with different concentrations for 5 min to partially replace the In on the electrode with Pd. After deposition, the 3D morphology of the electrodes was well preserved (Figure S15). Despite that the mass loading of Pd in the Pd-In electrodes is very low (in the range of 0.014 to 0.099

mg cm⁻² (Table S1)), Pd could homogenously distribute on the *hp*-In electrodes (Figure 6a). This is because Pd was mainly deposited on the surface of the electrodes. As shown in Figure 6b, the surface atomic ratios (XPS results) of Pd/In are much higher than the bulk atomic ratios (ICP-OES results).

The CO₂RR performance of the porous Pd–In electrodes were investigated at -0.7 V in CO₂ saturated 0.1 M KHCO₃ and the results are shown in Figure 6c. The performance of the hp-In electrode and an electrodeposited porous Pd electrode was also included for comparison. While hp-In displays a higher FE for formate (68.5%) than for CO (23.2%), after Pd deposition the formate FE declines systematically with an increase in the amount of Pd. In the meantime, the FE CO for Pd-In-1.0 sample increases to its highest value of ~70% and the total FE for CO₂RR approaches 90%. In contrast, the porous Pd electrode shows high activity towards HER instead of CO₂RR. Thus, despite the distinct chemical properties between Pd and Cu or Ag, we show here for the first time that Pd-In electrode can also be a highly selective CO₂-to-CO catalyst. Furthermore, the deposition of Pd also improves the catalytic activity. As shown in Figure 6c, the total current density dramatically increased from 2.5 mA cm⁻² for hp-In to 10 mA cm⁻² for Pd-In-2.0. These results not only indicate that the selectivity of the formate and CO can be tuned by deposition of Pd onto hp-In, but also suggest a promising strategy of using hp-In as a template for preparing other porous In-based bimetallic catalysts.

4. Conclusions

In summary, we have developed a porous 3D hierarchical In catalyst for selective CO_2RR by template-free electrodeposition of porous In onto a Cu mesh. The catalyst exhibits an extremely high formate production rate (1.14 mmol cm⁻² h⁻¹ at -1.2 V) and has excellent formate selectivity (~90%, from -1.0 to -1.2 V) as well as remarkable stability (24 h). The high catalytic activity is attributed to the highly porous hierarchical structure, which offers an enlarged surface area (27.6-fold higher than that of In foil). DFT calculations reveal that the preferential reduction of CO₂ to formate on the In electrodes originates from the intrinsic property of In, which prefers the stabilisation of *OCHO for formate production rather than *COOH or *H. Additional electrocatalytic studies indicate that the further improved formate selectivity on hp-In compared to In foil is strongly correlated with the highly porous morphology, which induces high local pH and therefore suppresses the evolution of H₂. Furthermore, the hp-In can also serve as a template for synthesising porous Pd-In electrodes to tune the formate/CO selectivity. Thus, the simple approaches for fabricating highly porous electrodes and the mechanistic insights for CO₂RR over nanostructured catalysts may provide guidelines for the design of other porous metal and alloy electrodes for large-scale CO₂RR applications.

Conflicts of interest

There are no conflicts to declare.

Chemistry A Accepted Manu

ot Materials

ARTICLE

Acknowledgements

This research is part of the activities of SCCER HeE, which is financially supported by Innosuisse-Swiss Innovation Agency. This research is also supported by SNF (Ambizione Project PZ00P2_179989). We thank Dr. Gian Luca De Gregorio and Prof. Raffaella Buonsanti for the analysis of liquid products using HPLC.

Notes and references

- J. H. Koh, D. H. Won, T. Eom, N. K. Kim, K. D. Jung, H. Kim,
 Y. J. Hwang and B. K. Min, *ACS Catal.*, 2017, 7, 5071–5077.
- H. Li, P. H. Opgenorth, D. G. Wernick, S. Rogers, T. Y. Wu,
 W. Higashide, P. Malati, Y. X. Huo, K. M. Cho and J. C. Liao, Science, 2012, 335, 1596.
- 3 C. Gimkiewicz, R. Hegner, M. F. Gutensohn, C. Koch and F. Harnisch, *ChemSusChem*, 2017, **10**, 958–967.
- 4 Y. Hori, Mod. Asp. Electrochem., 2008, 42, 89–189.
- 5 A. Komatsu, Seiji; Yanagihara, Tetsu; Hiraga, Yuki; Tanaka, Michie; Kunugi, *Denki Kagaku oyobi Kogyo Butsuri Kagaku*, 1995, **63**, 217–224.
- 6 R. Hegner, L. F. M. Rosa and F. Harnisch, *Appl. Catal. B* Environ., 2018, **238**, 546–556.
- 7 Z. M. Detweiler, J. L. White, S. L. Bernasek and A. B. Bocarsly, *Langmuir*, 2014, **30**, 7593–7600.
- J. L. White and A. B. Bocarsly, *J. Electrochem. Soc.*, 2016, 163, H410–H416.
- Z. Xia, M. Freeman, D. Zhang, B. Yang, L. Lei, Z. Li and Y.
 Hou, ChemElectroChem, 2018, 5, 253–259.
- 10 Z. Bitar, A. Fecant, E. Trela-Baudot, S. Chardon-Noblat and D. Pasquier, *Appl. Catal. B Environ.*, 2016, **189**, 172–180.
- 11 A. Rabiee and D. Nematollahi, *Mater. Chem. Phys.*, 2017, **193**, 109–116.
- 12 A. Dutta, M. Rahaman, N. C. Luedi, M. Mohos and P. Broekmann, ACS Catal., 2016, **6**, 3804–3814.
- 13 Y. Yoon, A. S. Hall and Y. Surendranath, *Angew. Chemie -Int. Ed.*, 2016, **55**, 15282–15286.
- 14 A. S. Hall, Y. Yoon, A. Wuttig and Y. Surendranath, *J. Am. Chem. Soc.*, 2015, **137**, 14834–14837.
- 15 J. E. Pander, M. F. Baruch and A. B. Bocarsly, *ACS Catal.*, 2016, **6**, 7824–7833.
- 16 C. I. Shaughnessy, D. T. Jantz and K. C. Leonard, *J. Mater. Chem. A*, 2017, **00**, 1–7.
- M. Liu, Y. Pang, B. Zhang, P. De Luna, O. Voznyy, J. Xu, X.
 Zheng, C. T. Dinh, F. Fan, C. Cao, F. P. G. de Arquer, T. S.
 Safaei, A. Mepham, A. Klinkova, E. Kumacheva, T. Filleter,
 D. Sinton, S. O. Kelley and E. H. Sargent, *Nature*, 2016, 537, 382–386.
- H. C. Shin, J. Dong and M. Liu, *Adv. Mater.*, 2003, **15**, 1610–1614.
- J. Liu, L. Cao, W. Huang and Z. Li, J. Electroanal. Chem., 2012, 686, 38–45.
- 20 C. W. Li and M. W. Kanan, J. Am. Chem. Soc., 2012, **134**, 7231–7234.
- A. D. J. Motheo, S. A. s. Machado, M. H. Van Kampen and J.
 R. S. Jr, J. Braz. Chem. Soc., 1993, 4, 122–127.

- 22 G. O. Larrazábal, A. J. Martín, S. Mitchell, R. Hauertrand Jrine Pérez-Ramírez, J. Catal., 2016, 343, 266–2079,39/C8TA11645H
- C. M. Gabardo, A. Seifitokaldani, J. P. Edwards, C. T. Dinh,
 T. Burdyny, M. G. Kibria, C. P. O'Brien, E. H. Sargent and D.
 Sinton, *Energy Environ. Sci.*, 2018, **11**, 2531–2539.
- 24 J. H. Kim, H. Woo, S. W. Yun, H. W. Jung, S. Back, Y. Jung and Y. T. Kim, *Appl. Catal. B Environ.*, 2017, **213**, 211–215.
- 25 Y.-C. Hsieh, S. D. Senanayake, Y. Zhang, W. Xu and D. E. Polyansky, *ACS Catal.*, 2015, **5**, 5349–5356.
- Z. Zhang, M. Chi, G. M. Veith, P. Zhang, D. A. Lutterman, J. Rosenthal, S. H. Overbury, S. Dai and H. Zhu, ACS Catal., 2016, 6, 6255–6264.
- A. Loiudice, P. Lobaccaro, E. A. Kamali, T. Thao, B. H.
 Huang, J. W. Ager and R. Buonsanti, *Angew. Chemie Int.* Ed., 2016, 55, 5789–5792.
- 28 G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, 54, 11169–11186.
- J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868.
- 30 P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953–17979.
- H. J. Monkhorst and J. D. Pack, *Phys. Rev. B*, 1976, 13, 5188–5192.
- A. A. Peterson, F. Abild-Pedersen, F. Studt, J. Rossmeisl and
 J. K. Nørskov, *Energy Environ. Sci.*, 2010, 3, 1311.
- J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R.
 Kitchin, T. Bligaard and H. Jónsson, J. Phys. Chem. B, 2004, 108, 17886–17892.
- W. Tang, A. A. Peterson, A. S. Varela, Z. P. Jovanov, L. Bech,
 W. J. Durand, S. Dahl, J. K. Nørskov and I. Chorkendorff,
 Phys. Chem. Chem. Phys., 2012, 14, 76–81.
- D. H. Won, C. H. Choi, J. Chung, M. W. Chung, E. H. Kim and
 S. I. Woo, *ChemSusChem*, 2015, 8, 3092–3098.
- W. Luo, W. Xie, R. Mutschler, E. Oveisi, G. L. De Gregorio, R.
 Buonsanti and A. Zuttel, ACS Catal., 2018, 8, 6571–6581.
- W. Lv, R. Zhang, P. Gao and L. Lei, J. Power Sources, 2014,
 253, 276–281.
- 38 J. Yu, H. Liu, S. Song, Y. Wang and P. Tsiakaras, Appl. Catal. A Gen., 2017, 545, 159–166.
- 39 F. Li, L. Chen, G. P. Knowles, D. R. MacFarlane and J. Zhang, Angew. Chemie Int. Ed., 2017, 56, 505–509.
- F. Lei, W. Liu, Y. Sun, J. Xu, K. Liu, L. Liang, T. Yao, B. Pan, S.
 Wei and Y. Xie, *Nat. Commun.*, 2016, 7, 1–8.
- S. Zhang, P. Kang and T. J. Meyer, J. Am. Chem. Soc., 2014, 136, 1734–1737.
- D. H. Won, C. H. Choi, J. Chung, M. W. Chung, E. H. Kim and
 S. I. Woo, *ChemSusChem*, 2015, 8, 3092–3098.
- B. Kumar, V. Atla, J. P. Brian, S. Kumari, T. Q. Nguyen, M.
 Sunkara and J. M. Spurgeon, *Angew. Chemie Int. Ed.*,
 2017, 56, 3645–3649.
- 44 D. Du, R. Lan, J. Humphreys, S. Sengodan, K. Xie, H. Wang and S. Tao, *ChemistrySelect*, 2016, **1**, 1711–1715.
- 45 N. Han, Y. Wang, H. Yang, J. Deng, J. Wu, Y. Li and Y. Li, *Nat. Commun.*, 2018, **9**, 1320.
 - H. Zhong, Y. Qiu, T. Zhang, X. Li, H. Zhang and X. Chen, *J. Mater. Chem. A*, 2016, **4**, 13746–13753.
 - N. Han, Y. Wang, H. Yang, J. Deng, J. Wu, Y. Li and Y. Li, *Nat. Commun.*, 2018, **9**, 1–8.

46

ARTICLE

View Article Online DOI: 10.1039/C8TA11645H

- 48 C. W. Lee, J. S. Hong, K. D. Yang, K. Jin, J. H. Lee, H. Y. Ahn,
 H. Seo, N. E. Sung and K. T. Nam, *ACS Catal.*, 2018, 8, 931–937.
- 49 J. Wang, H. Wang, Z. Han and J. Han, *Front. Chem. Sci. Eng.*, 2015, 9, 57–63.
- 50 M. Fan, S. Garbarino, G. A. Botton, A. C. Tavares and D. Guay, *J. Mater. Chem. A*, 2017, **5**, 20747–20756.
- W. Luc, C. Collins, S. Wang, H. Xin, K. He, Y. Kang and F. Jiao, J. Am. Chem. Soc., 2017, 139, 1885–1893.
- 52 X. Zhang, F. Li, Y. Zhang, A. M. Bond and J. Zhang, *J. Mater. Chem. A*, 2018, **6**, 7851–7858.
- S. Zhang, P. Kang, S. Ubnoske, M. K. Brennaman, N. Song,
 R. L. House, J. T. Glass and T. J. Meyer, *J. Am. Chem. Soc.*,
 2014, 136, 7845–7848.
- H. Wang, J. Jia, P. Song, Q. Wang, D. Li, S. Min, C. Qian, L.
 Wang, Y. F. Li, C. Ma, T. Wu, J. Yuan, M. Antonietti and G.
 A. Ozin, *Angew. Chemie Int. Ed.*, 2017, 56, 7847–7852.
- 55 H. Wang, Y. Chen, X. Hou, C. Ma and T. Tan, *Green Chem.*, 2016, **18**, 3250–3256.
- 56 J. Hussain, H. Jónsson and E. Skúlason, ACS Catal., 2018, 8, 5240–5249.
- 57 S. Back, M. S. Yeom and Y. Jung, ACS Catal., 2015, 5, 5089– 5096.
- W. Sheng, S. Kattel, S. Yao, B. Yan, Z. Liang, C. Hawxhurst,
 Q. Wu and J. G. Chen, *Energy Environ. Sci.*, ,
 DOI:10.1039/C7EE00071E.
- D. H. Won, H. Shin, J. Koh, J. Chung, H. S. Lee, H. Kim and S.
 I. Woo, Angew. Chemie Int. Ed., 2016, 55, 9297–9300.
- B. Jiang, X. G. Zhang, K. Jiang, D. Y. Wu and W. Bin Cai, J. Am. Chem. Soc., 2018, 140, 2880–2889.
- J. S. Yoo, R. Christensen, T. Vegge, J. K. Nørskov and F. Studt, *ChemSusChem*, 2016, 9, 358–363.
- J. T. Feaster, C. Shi, E. R. Cave, T. Hatsukade, D. N. Abram,
 K. P. Kuhl, C. Hahn, J. K. Nørskov and T. F. Jaramillo, ACS
 Catal., 2017, 7, 4822–4827.
- 63 Z. Zhao and G. Lu, ACS Catal., 2018, 3885–3894.
- 64 M. Karamad, V. Tripkovic and J. Rossmeisl, *ACS Catal.*, 2014, **4**, 2268–2273.
- S. Back, M. S. Yeom and Y. Jung, ACS Catal., 2015, 5, 5089– 5096.
- J. T. Feaster, C. Shi, E. R. Cave, T. Hatsukade, D. N. Abram,
 K. P. Kuhl, C. Hahn, J. K. Nørskov and T. F. Jaramillo, ACS
 Catal., 2017, 7, 4822–4827.
- E. L. Clark, J. Resasco, A. Landers, J. Lin, L. T. Chung, A.
 Walton, C. Hahn, T. F. Jaramillo and A. T. Bell, ACS Catal., 2018, 8, 6560–6570.
- 68 M. Ma, B. J. Trzesniewski, J. Xie and W. A. Smith, *Angew. Chemie - Int. Ed.*, 2016, **55**, 9748–9752.
- 69 A. S. Varela, M. Kroschel, T. Reier and P. Strasser, *Catal. Today*, 2016, **260**, 8–13.
- S. Rasul, D. H. Anjum, A. Jedidi, Y. Minenkov, L. Cavallo and
 K. Takanabe, *Angew. Chemie Int. Ed.*, 2015, 54, 2146–2150.
- 71 G. O. Larrazabal, A. J. Martin, S. Mitchell, R. Hauert and J. Perez-Ramirez, *J. Catal.*, 2016, **343**, 266–277.