



Porous multi-metallic Pt-based nanostructures as efficient electrocatalysts for ethanol oxidation: A mini-review

Adewale K. Ipadeola^{a,*}, Kamel Eid^{b,*}, Augustus K. Lebechi^c, Aboubakr M. Abdullah^a, Kenneth I. Ozoemena^c

^a Centre for Advanced Materials, Qatar University, Doha 2713, Qatar

^b Gas Processing Center (GPC), College of Engineering Qatar University, Doha 2713, Qatar

^c Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Private Bag 3, PO Wits, Johannesburg 2050, South Africa

ARTICLE INFO

Keywords:

Ethanol oxidation
Porous multi-metallic-Pt-nanostructures
Binary Pt-electrocatalysts
Ternary Pt-electrocatalysts
Ethanol fuel cells

ABSTRACT

Porous multi-metallic Pt-based nanostructures (PM-Pt-Ns) electrocatalysts possess various unique structural and compositional merits that facilitate their utilization in ethanol oxidation reaction (EOR), which is one of the most important parameters in ethanol-based fuel cells. Improving the EOR activity of PM-Pt-Ns electrocatalysts with low Pt-content remains a daunting challenge, so various efforts devoted to overcoming these barriers lie in controlling nanoparticle shapes/compositions using a variety of methods. This mini-review evaluates the most interesting papers related to PM-Pt-Ns (i.e., binary and ternary) electrocatalysts for EOR with annotations in the last three years. Different preparation methods, morphologies and compositions of PM-Pt-Ns electrocatalysts on the EOR activity are discussed, as well as the challenges for scalable fabrication of PM-Pt-Ns electrocatalysts as anodes for practical ethanol-based fuel cells. Finally, the prospects for directing the development of novel PM-Pt-Ns for practical applications are emphasized.

1. Introduction

The continuous usage of traditional fossil fuels leads to emissions of greenhouse gases which are the main drivers of global warming and climate challenges [1,2]. Various efforts were dedicated to solving this problem, like the conversion of such gases to usable hydrocarbon or less hazardous products (i.e., alcohol, glucose, etc) [3–5]. Ethanol-based fuel cells are green, cost-effective, efficient and renewable energy sources, owing to the low-cost, availability, ease of manipulation/storage of ethanol and great energy yield at low operating temperature [6–11]. Ethanol oxidation reaction (EOR) is the most important parameter of concern in an ethanol-based fuel cell that utilizes high-loading of Pt in different electrolytes (Fig. 1a). However, different attempts are being made to reduce the Pt-contents to a bare minimum, which led to the evolution of multi-metallic Pt-based electrocatalysts [12–15]. The EOR, in aqueous electrolytes and at low temperatures, has three expected products (acetaldehyde ($2e^-$), acetic acid ($4e^-$) and CO_2 ($12e^-$), Fig. 1b) with an energy barrier as illustrated in Fig. 1c. Amongst the products, acetic acid formation involving incomplete oxidation is the most predominant product (i.e., major product), particularly for multi-metallic

Pt-based materials, as it requires low energy and is facile compared to CO_2 formation (i.e., complete EOR, involving $12e^-$ and C–C cleavage). Hence, the mechanism of EOR for acetic acid formation ensures the decarbonization of the system, following two distinct steps: (i) oxidative dehydrogenation of ethanol to acetaldehyde and (ii) radical-autoxidation of acetaldehyde to acetic acid [16], owing to oxophilic/spill-over effects of the additional metals to Pt electrocatalysts, evidenced from high-resolution in-situ electrochemical NMR spectroscopy with interdigital electrodes studies [17,18].

Mixing Pt with one or two metals (i.e., alloy, core-shell and inter-metallic) with strategically tailored morphologies and modulated electronic structures are the main solutions for increased EOR activity, likewise reducing the consumption of earth-scarce and expensive Pt metal [6–11,19]. Porous multi-metallic Pt-based nanostructures (PM-Pt-Ns, i.e., binary and ternary) electrocatalysts possess various inimitable merits, like high surface area, low-density and accessible active sites, which accelerate the electron and mass transfer, enhance the adsorption of reactants and allow their diffusion into stable inner cavities during EOR [6–11]. Also, modulating the d-band centre of Pt by one or two metals upshift/downshift the Fermi level, which tunes the adsorption

* Corresponding authors.

E-mail addresses: ak.ipadeola@qu.edu.qa (A.K. Ipadeola), kamel.eid@qu.edu.qa (K. Eid).

<https://doi.org/10.1016/j.elecom.2022.107330>

Received 22 May 2022; Received in revised form 7 July 2022; Accepted 17 July 2022

Available online 23 July 2022

1388-2481/© 2022 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

energy of reactants/intermediates for higher EOR than monometallic Pt-based electrocatalysts [20–23]. Although porous tri-metallic Pt-based electrocatalysts are rarely reported, and always have superior activity than binary/mono Pt-based electrocatalysts. Notably, porous Pt-based electrocatalysts were reported to have significantly increased EOR resulting in nearly 159 published articles, however, only 70 published articles were reported for PM-Pt-Ns electrocatalysts in the last decade according to the Web-of-Science (as of April 30, 2022). So, it is important to be updated in this research area and further direct researchers' attention to the exploration of the interesting properties of these materials for EOR. Several reviews were published recently on porous Pt-based electrocatalysts for different applications [24–26]. However, a review on porous binary/ternary Pt-based nanostructure electrocatalysts for EOR is not yet reported, as the major challenges still lie on the fabrication approaches for tailoring the physical and chemical properties of porous Pt-based electrocatalysts [27–29]. The significance of this review is highlighted in Table 1 and compared with related articles.

Herein, recent advances on the fabrication of porous binary/ternary Pt-based electrocatalysts for EOR as a function of preparation methods, morphologies and compositions were discussed. This includes the annotations on the interesting papers related to PM-Pt-Ns with excellent EOR activity in the last three years, despite the existing barriers to the rational synthesis of PM-Pt-Ns as anodes for the large-scale EOR application. Finally, the prospects and suggestions for controlled synthesis of efficient and durable PM-Pt-Ns electrocatalysts for EOR at low Pt-content are emphasized to revitalize the attention of researchers in electrocatalysis for this application, that there are enormous porous Pt-based nanostructured electrocatalysts yet to be explored.

2. Preparation methods of PM-Pt-based electrocatalysts

Template-based, galvanic replacement (GR), solvo/hydrothermal, chemical-etching and chemical reductions are the main methods employed for the preparation of PM-Pt-Ns electrocatalysts. These are driven by various mechanisms, including continuous growth, crystallites coalescence, seeded growth route, Kirkendall effect, Ostwald ripening

Table 1

Comparative summary of previously reported reviews related to porous multi-metallic Pt-based electrocatalysts and the present study.

Title	Focus	Refs.
Porous multi-metallic Pt-based nanostructures as efficient electrocatalysts for ethanol oxidation: A mini-review	The current innovations in the strategic fabrication of porous binary/ternary Pt-based electrocatalysts with tailored morphologies and compositions for improved EOR in the last three years.	This work
Recent advances in porous Pt-based nanostructures: synthesis and electrochemical applications	The development of porous Pt-based nanostructured materials with emphasis on methanol oxidation reaction (MOR), EOR, oxygen reduction reaction (ORR) and glucose sensing.	[24]
Platinum-based ternary catalysts for the electrooxidation of ethanol	An overview of ternary Pt-based catalysts concerning their structure and compositions for direct ethanol fuel cells.	[26]

and dissolution-regrowth [24,30–34]. In continuous growth, metals with a higher redox potential are reduced to form nuclei, which serve as seeds and provide various nucleation sites for atoms of other metals in forming polyhedron shapes, like cubes, octahedrons and tetrahedrons [35]. In crystallite coalescence, a high reduction power is needed to promote the explosive nucleation forming multiple ultra-small energetic crystallites, reducing total surface energy and metal atoms diffusion across the interface to form nanocrystals [35]. In the seeded growth route, a metal seed serves as a support for the layered (at high lattice matching), island-like (at fast reduction kinetics) and intermediate growth of other metals [35]. In the Kirkendall effect, the occurrence of unequal diffusion among atomic species creates net vacancy flux that results in voids with tailored hollow structures [36]. In Ostwald ripening, large atoms grow at the expense of smaller atoms through the formation and decomposition of intermediate species that leads to nanoporous structures [37]. In dissolution-regrowth, hollow structure nanoparticles are formed from the self-limiting assembly of building

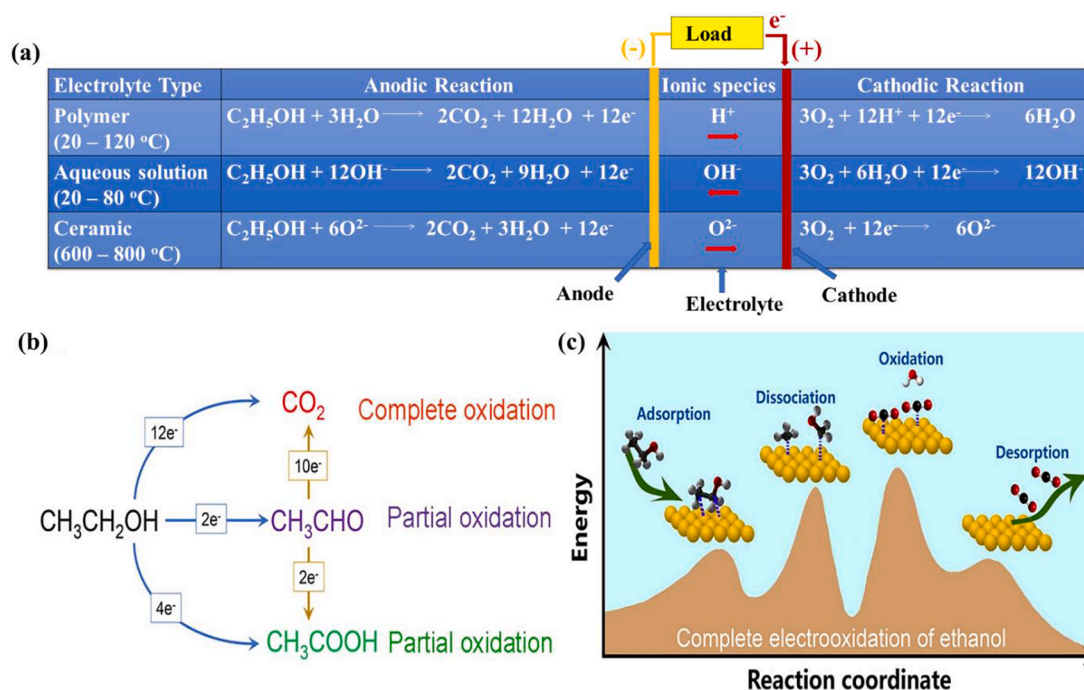


Fig. 1. (a) Ethanol-based fuel cell reactions in different electrolytes. Copyright 2021 the Royal Society of Chemistry Ref. [25] (b) Reaction pathways to C1 and C2 species and (c) Energy barrier for EOR. Copyright 2021 Elsevier Ref. [26].

blocks with controlled reorganization [38]. These methods are feasible with other methods, like solvothermal and GR. In GR, a metal seed with a lower redox potential reduces another metal with a higher redox potential via the initial adsorption of metal over seeds to allow subsequent electron transfer and diffusion of seeds into the solution [35]. The GR is tuned via surfactants and/or facet-specific agents to promote the growth of high-index facets. Reducing agent (i.e., NaBH_4 , ascorbic, and hydrazine), surfactant (i.e., Pluronic-F127, polyvinylpyrrolidone (PVP), cetyltrimethylammonium chloride (CTAC)), oxidants (i.e., O_2 and halides) and facet-directing agents (i.e., I and Br) are the main factors for realizing porosity [35,39,40]. Ordered porosity is achieved using hard templates (like anodic aluminium oxide) and mesoporous silica templates (i.e., FSM-16 and SBA-15), while non-order porosity is realized with soft templates (like PVP, CTAC and F127) [24,40–42].

3. Porous binary Pt-based electrocatalysts

Mixing Pt with another metal is an efficient way of promoting EOR activity than mono-Pt. Hierarchical 3D-PtPd/graphene nanosheets (3D-PtPd/GNS) at varied compositions were prepared by an electroless deposition over Cu-foam, followed by the chemical-vapour-deposition (CVD) that allowed GNS growth at 1000°C (25 min) and subsequently etched Cu with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ [43]. The formation mechanism of 3D-PtPd/GNS consisted of wrapping effect of the GNS on the PtPd nanoparticles (NPs). Significantly enhanced EOR was reported for 3D-Pt₅₁Pd₄₉/GNS compared to 3D-Pt₆₁Pd₃₉/GNS, 3D-Pt₃₆Pd₆₄/GNS, 3D-Pt/GNS and Pt black by at least 1.6 times, due to its 3D continuous and non-order porous structure and excellent uniform dispersion that influenced its more accessible active sites, high electrochemically active surface area

(ECSA = $87.9\text{ m}^2/\text{g}$), fast charge-transfer and good tolerance to CO poisoning.

Microemulsion/impregnation/chemical-reduction methods were used to prepare Pt/Ni(OH)₂ nanoflakes, achieved by the formation of micelles/nuclei and then growth using organic surfactant/solvent, which its high porosity with well-dispersed Pt facilitated abundant active, high intrinsic surface area and ions mobility for excellent EOR activity and stability [44]. A dynamic gas bubble template method was employed to prepare Pt on honeycomb-like porous Au_H/Au (Pt/Au_H/Au) [45]. The formation mechanism of Pt/Au_H/Au consisted of simultaneous electrodeposition of Pt on Au and gas evolution, and thus showed EOR of 5.1, 10.5 and 13.5 times to Pt/Au_{c-3}/Au, Pt/Au_{c-1}/Au and Pt/Au, respectively, because of its unique morphology and porosity that affected its high surface area and active sites with fast electron/mass transfer and low impedance for facile EOR. Electrospun Pt-SnO₂/carbon nanofiber (Pt-SnO₂/CNF) was achieved with polyacrylonitrile (PAN) and polyvinylidene fluoride (PVDF) as a carrier and pore-forming agents, respectively [46]. The formation mechanism of Pt-SnO₂/CNF encompassed wrapping of the Pt-SnO₂ nanoparticles on the CNF support during electrospinning. The porous structure of Pt-SnO₂/CNF with PVDF at an optimized ratio (1:0.8) provided more active sites, surface area, facile charge mobility and low chemical resistance that endeared its electrocatalysis of 3.3 times more than Pt/SnO₂/CNF without PVDF, thus, its superior EOR with high ECSA ($54.30\text{ m}^2/\text{g}$) and specific activity ($140.14\text{ mA}/\text{cm}^2$). Magnus's salt ($[\text{PtCl}_4]^{2-}$ with $[\text{Pt}(\text{NH}_3)_4]^{2+}$ and $[\text{Cu}(\text{NH}_3)_4]^{2+}$) needle template method at varied ratios (1:1:0, 2:1:1, 3:1:2, and 1:0:1) was adopted to synthesize hierarchically porous Pt-Cu macrobeams through chemical reduction with dimethylamine borane (DMAB) or NaBH_4 (Fig. 2a) [47]. Pt/Cu (3:1:2) utilized DMAB possessed

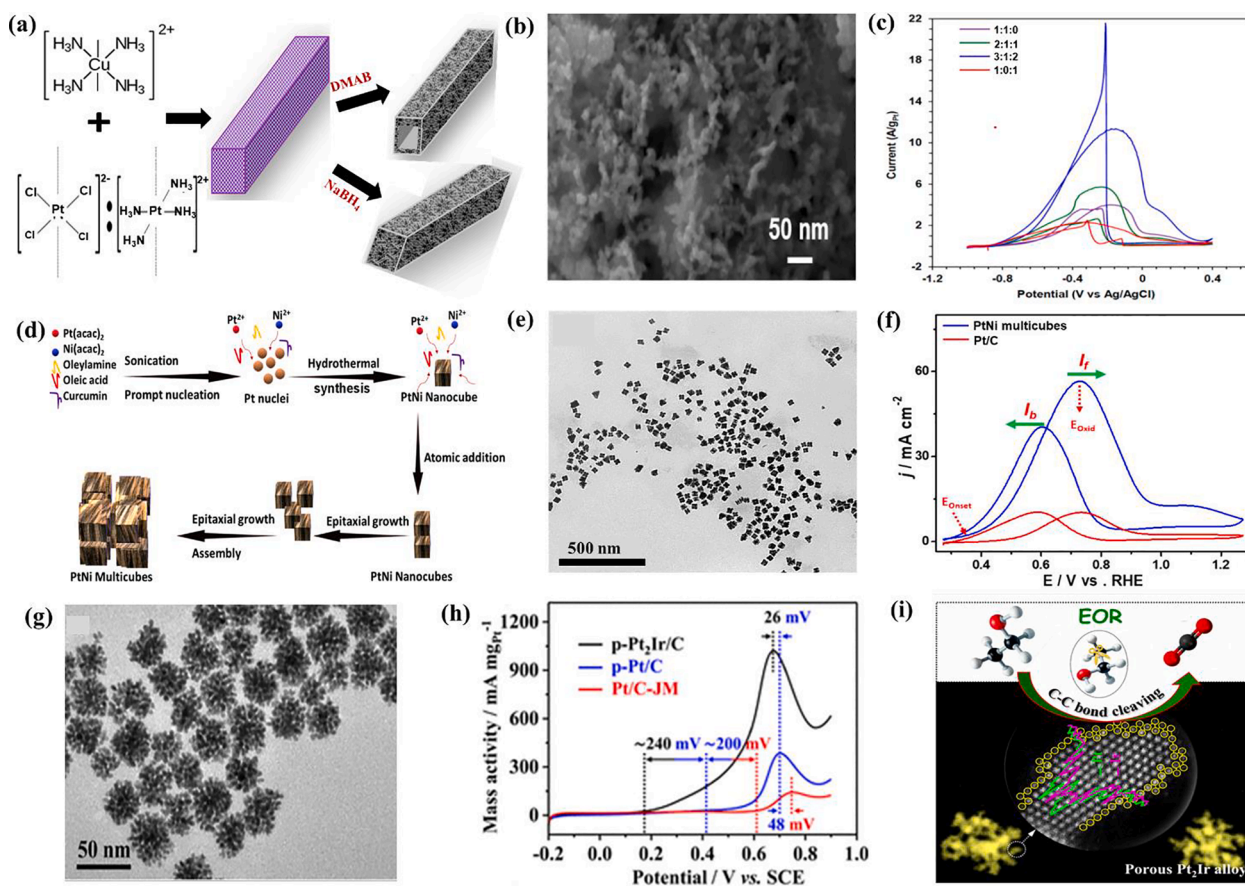


Fig. 2. (a) Chemical reduction synthetic scheme, (b) TEM and (c) EOR CV of macrobeam Pt/Cu. MDPI Ref. [47], (d) Template-free solvothermal synthetic scheme, (e) concentric multicube morphology and (f) EOR CV of PtNi, (g) nanocrystal TEM image, (h) EOR CV, and (i) EOR mechanism of Pt₂Ir/C. Copyright 2020, 2021 American Chemical Society Refs. [50,52].

combined microtube and macrobeam structures (Fig. 2b) and showed the best EOR amongst other ratios (Fig. 2c) and those prepared with NaBH_4 , due to its highly porous structure that made Pt and Cu more accessible during the EOR. The formation method of porous Pt/Cu macrobeams or macrotubes originated from the charge balance dissolution mechanism during the reduction process. Thermally synthesized metal-organic framework (MD-PtCo/C allowed Pt^{4+} to replace partially dispersed Co^{2+} from $\text{Co}_3[\text{Co}(\text{CN})_6]_2$ precursor [48]. MD-PtCo/C fabrication mechanism involved in-situ reduction of gases for Pt/Co nanoparticles anchorage on C-N co-ordinating network during decomposition. MD-PtCo/C gave an EOR activity that was 1.57 times more than commercial Pt/C because of its increased electron transfer, dispersed active sites and optimal Pt utilization, traced to N from CN-linkers, Co dispersed sites and moderately diffused Pt into $\text{Co}_3[\text{Co}(\text{CN})_6]_2$ frameworks, respectively. 3D porous PtSn with tailored compositions (81:19; 73:27; and 67:33) were synthesized via a liquid-phase reduction process driven by the Ostwald ripening growth mechanism, where Pt/Sn atoms first nucleated from the metal salts and then grew to Pt/Sn NPs using NaBH_4 reducing agent [49]. $\text{Pt}_{73}\text{Sn}_{27}$ had a unique interconnected and 3D porous structure that induced rich active sites, external carriers, synergistic effects and prolonged Sn leaching that are beneficial for its high EOR activity and excellent CO-tolerance without morphological change compared to $\text{Pt}_{81}\text{Sn}_{19}$, $\text{Pt}_{67}\text{Sn}_{33}$ and Pt/C. Template-free solvothermally synthesized cocentric PtNi multicubes (Fig. 2d) at varied oleylamine/oleic acid ratios with curcumin, had multi-dimensional nano-architectonics morphology (Fig. 2e), high-index facets and alloying effects that maximally utilized Pt for high EOR activity with specific activities of 9.03 times than Pt/C (Fig. 2f) [50]. The formation mechanism of PtNi multicubes was attributed to the

in-situ isolation of nucleation from the oriented attachment of epitaxial growth. Pt/ $\text{Bi}(\text{OH})_3$ nanoframes prepared by a solvothermal method revealed porous nanostructure, which influenced its increased surface area and copious defects that led to EOR mass activity of 13.5 times more than commercial Pt/C and exceptional stability [51]. The production mechanism of Pt- $\text{Bi}(\text{OH})_2$ involved electrochemical leaching of Bi atoms and oxidation of Bi^0 residual to Bi^{3+} in the form of $\text{Bi}(\text{OH})_3$. Wet-chemical reduction method was used to prepare porous-Pt₂Ir/C nanocrystals with interconnected 1D rough branches (Fig. 2g), which boosted the EOR activity (Fig. 2h) by 3.1 and 7.2 times those of p-Pt/C and commercial Pt/C-JM, respectively [52]. This was due to the unique porous features of p-Pt₂Ir/C (i.e., atomic steps/corners, abundant and accessible active sites) which accelerated mass transfer, enhanced CO-tolerance, eased cleavage of C—C bond and maximized the utilization of Pt/Ir during EOR. Notably, the fabrication process of p-Pt₂Ir/C was based on the crystallites' coalescence mechanism, due to the high reduction power of ascorbic acid under sonication, meanwhile octadecene acts as a template to drive formation of porous branched shape. A proposed mechanism of EOR on p-Pt₂Ir/C revealed facile C—C cleavage for C1 product formation (Fig. 2i), although this claim was not experimentally supported by an in-situ products formation studies.

4. Ternary Pt-based electrocatalysts

Porous ternary Pt-based electrocatalysts are the most promising for EOR than binary and mono Pt-based electrocatalysts. Porous PtRhCu cubic nano-boxes at different compositions were synthesized by a GR method (Fig. 3a), where Pt^{2+} gained e^- from Cu_2O to yield Pt nanocrystals, which subsequently reduced Rh^{3+} catalytically and then

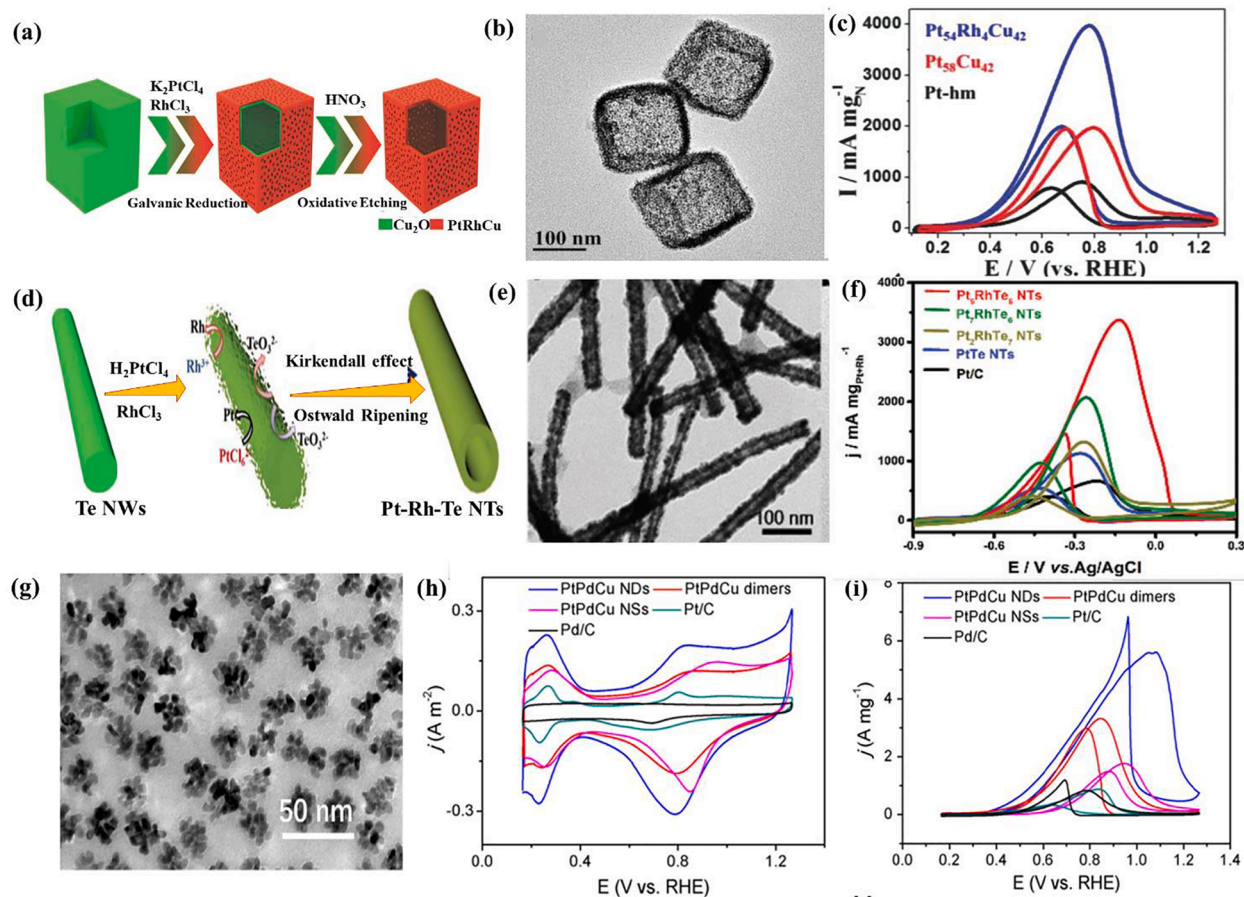


Fig. 3. (a) Galvanic reduction/oxidative etching synthetic scheme, (b) TEM, and (c) EOR of $\text{Pt}_{54}\text{Rh}_4\text{Cu}_{42}$, $\text{Pt}_{54}\text{Cu}_{42}$ and Pt-hm. Copyright 2018 Wiley-VCH Ref. [53], (d) Self-template method involving Kirkendall effect and Oswald ripening, (e) TEM, and (f) EOR of PtRhTe derivatives. Copyright 2018 the Royal Society of Chemistry Ref. [55], (g) TEM, (h) CV in KOH only (i) EOR activities of PtPdCu (different morphologies), Pd/C and Pt/C. Copyright 2020 Elsevier Ref. [56].

oxidative etching [53]. The fabrication process of PtRhCu nanocrystals comprised the reduction of Pt^{2+} by Cu_2O to produce Pt nuclei following Nernst equilibrium potential, then subsequently reduction of Rh^{3+} by the Pt nuclei following catalytic growth and simultaneous diffusion of Pt, Rh and Cu atoms. The porous feature of $\text{Pt}_{54}\text{Rh}_4\text{Cu}_{42}$ with nano-boxes morphology (Fig. 3b), induced increased surface area and ionic mobility that resulted in significantly high EOR mass activities by 1.6 and 2.3 than $\text{Pt}_{58}\text{Cu}_{42}$ and Pt-hm (Fig. 3c). PtPdNi nanoparticles were prepared by galvanic replacement on different carbon supports: (i) biomass-derived activated carbons (PtPdNi/a-BC and PtPdNi/b-BC), (ii) nano-casted ordered micro-mesoporous (NOM) carbon (PtPdNi/CMK-3) and (iii) carbon black (PtPdNi/Vulcan) [54]. The fabrication method of porous PtPdNi on the carbon supports involved the simultaneous dissolution of the Pt, Pd and Ni atoms, where the Ni atom enabled the co-reduction of both Pt and Pd ions for explosive nucleation, growth and coalescence of PtPdNi voids. PtPdNi/CMK-3 (302 mA/mg) showed high EOR than PtPdNi/a-BC (202 mA/mg), PtPdNi/b-BC (217 mA/mg) and PtPdNi/Vulcan (202 mA/mg). The suitability of NOM support was attributed to its porous nature with uniformly dispersed nanoparticles and ease of mass transport of reactants/intermediates. Self-templated 1D PtRuTe nanotubes were prepared at varied compositions (5:1:6; 7:1:6 and 2:1:7) following the Kirkendall effect and Oswald ripening (Fig. 3d) [55]. The formation process of porous PtRuTe involved unequally diffusion of Pt, Ru and Te vapours to form a net vacant flux of voids and concurrent growth of Pt on Ru/Te atoms via the formation and decomposition of intermediation metals' ions species to form hollow nanostructures. The porous Pt_5RuTe_6 had unique tubular morphology (Fig. 3e) with more exposed active surfaces for quick adsorption/desorption of reactive species and thus increased its EOR activity by 1.6, 2.5, 3.0 and 5.1 times to Pt_7RuTe_6 , Pt_2RuTe_7 , PtTe and Pt/C, respectively (Fig. 3f). PtPdCu nanocrystals, with different morphologies: nanodendrites (NDs, (Fig. 3g), dimers and nanosphere (NS)), PtPd and PtCu were hydrothermally synthesized [56]. The porous PtPdCu formation mechanism comprised co-reduction of the metal ions with PVP, while potassium iodide (KI) directed the nanocrystals' structures by slow reduction kinetics for the complexation of I^- ions with Pd precursor and oxidative etching effect of I^-/O_2 during nanocrystals growth. The porosity of PtPdCu NDs influenced stepped surfaces that provided abundant active sites with facile diffusion of reactive species, high surface to volume ratio, reduced ionic and mass transfer resistance and strong synergy for excellent EOR amongst others with enhanced mass and specific activities of 6.4 and 3.6 times the commercial Pt/C (Fig. 3h and 3i). Pulsed-laser-deposition of trilayered Rh/Pt/SnO₂/CP at varied Rh compositions (0, 5, 10, 20 and 50) were synthesized [57]. The porous Rh/Pt/SnO₂ trilayered nanocrystals were formed on carbon paper (CP) support in a stepwise manner of high power laser absorption of the Rh, Pt and Sn ions, formation of the plasma plume, deposition of the plasma plume on CP, nucleation and growth of the Rh/Pt/SnO₂ films. Rh₅/Pt/SnO₂/CP (179.2 mA/mg) gave boosted EOR activity and CO-tolerance compared to Rh₁₀/Pt/SnO₂/CP (142.0 mA/mg), Rh₂₀/Pt/SnO₂/CP (149.9 mA/mg), Rh₅₀/Pt/SnO₂/CP (108.8 mA/mg), binary counterparts and Pt/CP(79.5 mA/mg) because the porosity of Rh₅/Pt/SnO₂/CP impelled enhanced OH⁻ promotional effects by both Rh and SnO₂, ease of ions diffusion and charge transfer, in addition to facile C—C cleavage by the lowest thickness of Rh (low amount). The synthetic approaches, morphologies and EOR activities of PM-Pt-Ns electrocatalysts in the last three years are summarized in Table 2. Moreover, the use of computational simulations will be a great deal of assistance in strategically designing suitable PM-Pt-Ns to establish structures, morphologies, compositions and EOR electrocatalysis relationships, prior to experimental synthesis and applications [58–60].

5. Conclusions and future perspectives

This article summarizes the recent advances in the controlled fabrication of porous binary and ternary Pt-based nanostructure

Table 2

Comparison of the EOR activities on PM-Pt-Ns electrocatalysts in the last three years. *Refers to the specific activity.

Catalysts	Morphology	Synthetic methods	Mass/ Specific Activity	Refs.
3D $\text{Pt}_{51}\text{Pd}_{49}$ /GNS	3D-hierarchical nanosheets	Electroless deposition and Chemical-vapour-deposition	*0.030 A/cm ² @-0.15 V _{Ag/AgCl}	[43]
Pt/Ni(OH) ₂	Nanoflakes	Microemulsion/impregnation/chemical-reduction	n.a	[44]
Pt/Au _H /Au	3D honey-comb like	Dynamic gas bubble template	*0.182 A/cm ² @0.9 V _{SCE}	[45]
Pt-SnO ₂ /CNF (1:0.8)	Nanofiber	Electrospinning	0.305A/mg _{Pt} ; 0.140 A/cm ² @0.9 V _{SCE}	[46]
Pt ²⁺ :Pt ²⁺ :Cu (DMAB,3:1:2)	Macrobeams and macrotubes	Magnus's salt needle salt-template	12.0 A/g _{Pt} @-0.20 V _{Ag/AgCl}	[47]
MD-PtCo/C	Nanoporous	Annealing	0.85 A/mg _{Pt} @0.0 V _{Ag/AgCl}	[48]
Pt ₇₃ Sn ₂₇	3D nanostructure	Liquid-phase reduction	≈ 0.4 A mg _{Pt} ⁻¹ @0.8 V _{SCE}	[49]
PtNi	Multicubes	Template-free solvothermal	0.0013 A/cm ² ; 2.86 A/mg _{Pt}	[50]
Pt-Bi(OH) ₃	Nanoframes	Solvothermal	@0.7 V _{RHE} 6.87 A/mg _{Pt} @-0.30 V _{SCE}	[51]
p-Pt ₂ Ir/C	Nanocrystals	Wet-chemical reduction	1.019 A/mg _{Pt} @-0.70 V _{SCE}	[52]
$\text{Pt}_{54}\text{Rh}_4\text{Cu}_{42}$	Cubic nanoboxes	GR	*15 mA/cm ² , 4 A/g _{Pt} @0.8 V _{RHE}	[53]
$\text{Pt}_{65}\text{Pd}_{25}\text{Ni}_{15}$ /CMK-3	Hierarchical porosity	GR	0.302 A/mg _{Pt} @-0.20 V _{Ag/AgCl}	[54]
Pt ₅ RhTe ₆	1D nanotubes	Self-template	AgCl 3.37 A/mg _{Pt+Rh} @-0.15 V _{Ag/AgCl}	[55]
PtPdCu NDs	Nanodendrites	Hydrothermal	AgCl 5.59 A/mg _{PtPd} ; *0.0158 A/cm ² @1.1 V _{RHE}	[56]
Rh ₅ /Pt/SnO ₂	Porous tri-layered	Pulsed-laser-deposition	*0.0215 A/cm ² ; 0.179 A/mg _{Pt} @0.70 V _{Ag/AgCl}	[57]

electrocatalysts for excellent EOR activity in the last three years. Porous binary $\text{Pt}_{51}\text{Pd}_{49}$ /GNS, Pt/Ni(OH)₂, Pt/Au_H/Au, Pt-SnO₂/CNF, Pt²⁺:Pt²⁺:Cu, MD-PtCo/C, PtPd, Pt₇₃Sn₂₇, PtNi, Pt-Bi(OH)₃, and p-Pt₂Ir/C were synthesized for EOR using various methods, like template-based, chemical-reduction, and solvothermal. Pt-Bi(OH)₃ displayed the highest reported mass activity of 6.87 A/mg_{Pt}, due to the porous nanostructure, increased surface area and copious defects. Porous ternary $\text{Pt}_{54}\text{Rh}_4\text{Cu}_{42}$, $\text{Pt}_{65}\text{Pd}_{25}\text{Ni}_{15}$ /CMK-3, Pt₅Rh₆Te-NTs and PtPdCu-NDs nanodendrites were prepared by GR, template, and hydrothermal methods, respectively, and tested for EOR. PtPdCu NDs showed the highest mass activity of (5.59 A/g_{PtPd}), due to the great synergy and unique features of porous dendritic shape, which maximized the atomic utilization during EOR.

Notably, tri-metallic Pt-based catalysts are rarely reported compared to bi-metallic Pt-based for EOR. This is plausibly due to the complications related to the reduction kinetics of three-metals with dissimilar atomic radii, electronic structures, and redox potential besides their mutual interaction with surfactants. Porous ternary Pt-catalysts are deemed the best electrocatalysts for EOR, as multiple electronic effects (i.e., strain and synergism) are merged with the exceptional structural features (i.e., great surface area, low density and maximized atom utilization). The rational design of PM-Pt-Ns electrocatalysts for EOR is not well-studied: as only 17 articles were published in the last three years. Hence, the attention of researchers in electrocatalysis is directed toward exploring these interesting materials for ethanol electrooxidation. Moreover, in-situ studies of EOR on PM-Pt-Ns electrocatalysts are necessary to reveal/confirm the most preferred product formed rather than speculating that CO₂ is the major product, as this would further corroborate the decarbonization and renewability of ethanol-based fuel cells.

From an outlook view, further studies are highly needed to develop simple, one-step, template-free and green methods for high mass-production (several grams in one run) of PM-Pt-Ns electrocatalysts at room temperature to allow their utilization in large-scale applications. This could be achieved via strong/mild reductants for three/two metals with relatively close redox potential in the presence of water-soluble copolymers (i.e., PVP, CTAB, and Brij) as structural directing agents. Considering the distinct physicochemical merits of high-entropy alloys (HEA), porous Pt-based HEA electrocatalysts should be an interesting area to be explored for EOR, as no studies have been reported so far. The in-situ growth of PM-Pt-Ns electrocatalysts over solid substrates, like carbon paper, carbon cloth and Ni-foam, should be explored to allow their feasibility for practical applications. Also, computational simulation should be coupled with experimental studies to further sort out the relationship between EOR performance and the structure of PM-Pt-Ns electrocatalysts, as well as understand their pathway or mechanism.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

This work was supported by the Qatar University Internal Grant (QUHI-CAM-22/23-550), Qatar National Research Fund (NPRP13D-0117-200095), and South African National Research Foundation (NRF) through the NRF/DSI/Wits SARChI Chair in Materials Electrochemistry and Energy Technologies (MEET) (UID No. 132739). Open Access funding provided by the Qatar National Library.

References

- J. Lelieveld, K. Klingmüller, A. Pozzer, R. Burnett, A. Haines, V. Ramanathan, *Proc. Natl. Acad. Sci. USA* 116 (2019) 7192–7197.
- M. Zhang, J. Zhang, S. Ran, W. Sun, Z. Zhu, *Electrochem. Commun.* 138 (2022), 107283.
- Q. Lu, K. Eid, W. Li, A.M. Abdullah, G. Xu, R.S. Varma, *Green Chem.* 23 (2021) 5394–5428.
- K.I. Ozoemena, S. Musa, R. Modise, A.K. Ipadeola, L. Gaolatlhe, S. Peteni, G. Kabongo, *Curr. Opin. Electrochem.* 10 (2018) 82–87.
- N.E. Mphahlele, A.K. Ipadeola, A.B. Haruna, P.V. Mwangi, R.M. Modibedi, N. Palaniandy, C. Billing, K.I. Ozoemena, *Electrochim. Acta* 409 (2022), 139977.
- A.K. Ipadeola, R. Barik, S.C. Ray, K.I. Ozoemena, *Electrocatalysis* 10 (2019) 366–380.
- A.K. Ipadeola, N.Z.L. Mathebula, M.V. Pagliaro, H.A. Miller, F. Vizza, V. Davies, Q. Jia, F. Marken, K.I. Ozoemena, *ACS Appl. Energy Mater.* 3 (2020) 8786–8802.
- K. Eid, Y.H. Ahmad, H. Yu, Y. Li, X. Li, S.Y. AlQaradawi, H. Wang, L. Wang, *Nanoscale* 9 (2017) 18881–18889.
- X. Gu, C. Wang, L. Yang, C. Yang, J. Nanosci Nanotechnol. 17 (2017) 2843–2847.
- K. Zhang, H. Xu, B. Yan, J. Wang, Z. Gu, Y. Du, *Appl. Surf. Sci.* 425 (2017) 77–82.
- A. Rodríguez-Gómez, E. Lepre, L. Sánchez-Silva, N. López-Salas, A.R. de la Osa, *J. Energy Chem.* 66 (2022) 168–180.
- F. Gao, Y. Zhang, Z. Wu, H. You, Y. Du, *Coord. Chem. Rev.* 436 (2021), 213825.
- Y. Zhang, F. Gao, H. You, Z. Li, B. Zou, Y. Du, *Coord. Chem. Rev.* 450 (2022), 214244.
- F. Gao, Y. Zhang, F. Ren, Y. Shiraiishi, Y. Du, *Adv. Funct. Mater.* 30 (2020) 2000255.
- J.J. Ogada, A.K. Ipadeola, P.V. Mwangi, A.B. Haruna, F. Nichols, S. Chen, H. A. Miller, M.V. Pagliaro, F. Vizza, J.R. Varcoe, D.M. Meira, D.M. Wamwangi, K. I. Ozoemena, *ACS Catal.* 12 (2022) 7014–7029.
- S. Mostrou, A. Nagl, M. Ranocchiari, K. Föttinger, J.A. van Bokhoven, *ChemComm.* 55 (2019) (1836) 11833–11841.
- E.G. Sorte, S. Jilani, Y.J. Tong, *Electrocatalysis* 8 (2017) 95–102.
- O. Guillén-Villafuerte, G. García, M.C. Arévalo, J.L. Rodríguez, E. Pastor, *Electrochem. Commun.* 63 (2016) 48–51.
- A.K. Ipadeola, A.K. Lebechi, L. Gaolatlhe, A.B. Haruna, M. Chitt, K. Eid, A. M. Abdullah, K.I. Ozoemena, *Electrochem. Commun.* 136 (2022), 107207.
- T.J. Wang, Y.C. Jiang, J.W. He, F.M. Li, Y. Ding, P. Chen, Y. Chen, *Carbon Energy* 4 (2022) 283–293.
- T.-J. Wang, H.-Y. Sun, Q. Xue, M.-J. Zhong, F.-M. Li, X. Tian, P. Chen, S.-B. Yin, Y. Chen, *Sci. Bull.* 66 (2021) 2079–2089.
- T.J. Wang, F.M. Li, H. Huang, S.W. Yin, P. Chen, P.J. Jin, Y. Chen, *Adv. Funct. Mater.* 30 (2020) 2000534.
- A.K. Ipadeola, P.V. Mwangi, K.I. Ozoemena, *Electrochim. Acta* 390 (2021), 138860.
- Y. Xu, B. Zhang, *Chem. Soc. Rev.* 43 (2014) 2439–2450.
- L. Yaqoob, T. Noor, N. Iqbal, *RSC Adv.* 11 (2021) 16768–16804.
- G. Yang, Q. Zhang, H. Yu, F. Peng, *Particulology* 58 (2021) 169–186.
- J. Bai, D. Liu, J. Yang, Y. Chen, *ChemSusChem* 12 (2019) 2117–2132.
- J. Bai, X. Xiao, Y.-Y. Xue, J.-X. Jiang, J.-H. Zeng, X.-F. Li, Y. Chen, *A.C.S. Appl. Mater. Interfaces* 10 (2018) 19755–19763.
- H. Liu, J. Li, L. Wang, Y. Tang, B.Y. Xia, Y. Chen, *Nano Res.* 10 (2017) 3324–3332.
- S. Lu, K. Eid, Y. Deng, J. Guo, L. Wang, H. Wang, H. Gu, *J. Mater. Chem. A* 5 (2017) 9107–9112.
- Q. Lu, H. Wang, K. Eid, Z.A. Allothman, V. Malgras, Y. Yamauchi, L. Wang, *Chem. Asian J.* 11 (2016) 1939–1944.
- L. Sun, H. Wang, K. Eid, S.M. Alshehri, V. Malgras, Y. Yamauchi, L. Wang, *Electrochim. Acta* 188 (2016) 845–851.
- K. Eid, H. Wang, V. Malgras, Z.A. Allothman, Y. Yamauchi, L. Wang, *J. Phys. Chem. C* 119 (2015) 19947–19953.
- S. Lu, K. Eid, M. Lin, L. Wang, H. Wang, H. Gu, *J. Mater. Chemistry A* 4 (2016) 10508–10513.
- J. Gu, Y.-W. Zhang, F.F. Tao, *Chem. Soc. Rev.* 41 (2012) 8050–8065.
- A.-A. El Mel, R. Nakamura, C. Bittencourt, Beilstein *J. Nanotechnol.* 6 (2015) 1348–1361.
- C.J. Gommers, *Nanoscale* 11 (2019) 7386–7393.
- M. Lin, H. Huang, Z. Liu, Y. Liu, J. Ge, Y. Fang, *Langmuir* 29 (2013) 15433–15441.
- K. Eid, H. Wang, V. Malgras, S.M. Alshehri, T. Ahamad, Y. Yamauchi, L. Wang, *J. Electroanal. Chem.* 779 (2016) 250–255.
- K. Eid, H. Wang, V. Malgras, Z.A. Allothman, Y. Yamauchi, L. Wang, *Chem. Asian J.* 11 (2016) 1388–1393.
- H. Zhang, H. Wang, K. Eid, L. Wang, *Part. Part. Syst. Charact.* 32 (2015) 863–868.
- B.T. Jebaslinhepzybai, N. Prabu, M. Sasidharan, *Int. J. Hydrog. Energy* 45 (2020) 11127–11137.
- H. Van Hien, T.D. Thanh, N.D. Chuong, D. Hui, N.H. Kim, J.H. Lee, *Compos. B. Eng.* 143 (2018) 96–104.
- Z. Yan, M. Lu, Q. Li, L. An, Z. Xu, L. Zhu, *Curr. Nanosci.* 15 (2019) 242–247.
- K. Jin, F. He, Q. Xie, *J. Electroanal. Chem.* 849 (2019), 113375.
- X. Wang, X. Hu, J. Huang, W. Zhang, W. Ji, Y. Hui, X. Yao, *Solid State Sci.* 94 (2019) 64–69.
- F.J. Burpo, E.A. Nagelli, A.R. Losch, J.K. Bui, G.T. Forcherio, D.R. Baker, J. P. McClure, S.F. Bartolucci, D.D. Chu, *Catalysts* 9 (2019) 662.
- W. Wang, X. Liu, Y. Wang, L. Zhang, S. Imhanria, Z. Lei, *J. Taiwan Inst. Chem. Eng.* 104 (2019) 284–292.
- Y. Sun, H. Xiang, H. Li, G. Yu, H. Chen, S. Liu, *Chin. Chem. Lett.* 31 (2020) 2491–2494.
- F. Wu, K. Eid, A.M. Abdullah, W. Niu, C. Wang, Y. Lan, A.A. Elzatahry, G. Xu, A.C. S. Appl. Mater. Interfaces 12 (2020) 31309–31318.
- X. Yuan, B. Jiang, M. Cao, C. Zhang, X. Liu, Q. Zhang, F. Lyu, L. Gu, Q. Zhang, *Nano Res.* 13 (2020) 265–272.
- Y. Fang, D. Cao, Y. Shi, S. Guo, Q. Wang, G. Zhang, P. Cui, S. Cheng, *J. Phys. Chem. Lett.* 12 (2021) 6773–6780.
- S.H. Han, H.M. Liu, P. Chen, J.X. Jiang, Y. Chen, *Adv. Energy Mater.* 8 (2018) 1801326.
- J.J. Arroyo-Gómez, D. Barrera, R.M. Castagna, J.M. Sieben, A.E. Alvarez, M.M. E. Duarte, K. Sapag, *ChemCatChem* 11 (2019) 3451–3464.
- L. Jin, H. Xu, C. Chen, H. Shang, Y. Wang, C. Wang, Y. Du, *Inorg. Chem. Front.* 7 (2020) 625–630.
- F. Wang, K. Wang, C. An, C. An, W. Zhang, *J. Colloid Interface Sci.* 571 (2020) 118–125.
- H. Wang, S. Sun, M. Mohamedi, *Energy Technol.* 9 (2021) 2000949.

- [58] S. Dai, T.-H. Huang, X. Yan, C.-Y. Yang, T.-Y. Chen, J.-H. Wang, X. Pan, K.-W. Wang, *ACS Energy Lett.* 3 (2018) 2550–2557.
- [59] C. Wang, H. Xu, F. Gao, Y. Zhang, T. Song, C. Wang, H. Shang, X. Zhu, Y. Du, *Nanoscale* 11 (2019) 18176–18182.
- [60] N. Erini, R. Loukrakpam, V. Petkov, E.A. Baranova, R. Yang, D. Teschner, Y. Huang, S.R. Brankovic, P. Strasser, *ACS Catal.* 4 (2014) 1859–1867.