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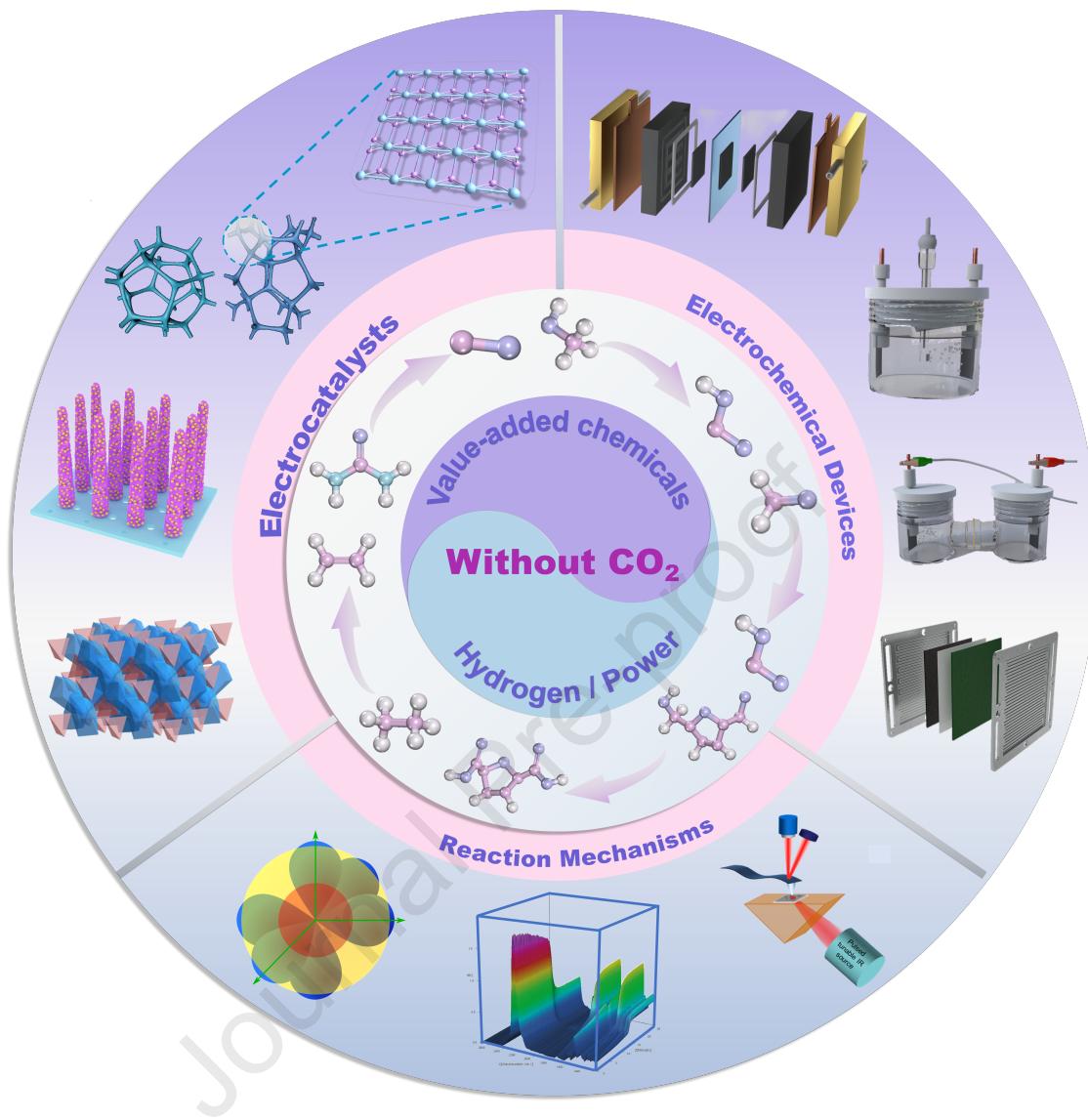
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Electrochemical conversion of small organic molecules to value-added chemicals and hydrogen/electricity without CO₂ emission: electrocatalysts, devices and mechanisms

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Abstract

The electrochemical conversion of small organic molecules to value-added chemicals and hydrogen/electricity without CO₂ emissions integrates efficient energy conversions (hydrogen energy or electricity) and value-added chemical productions in one reaction system, which is essentially competitive in the carbon-neutral era. However, the activity, stability, and cost-effectiveness of electrocatalysts, as well as the safety, durability, and scalability of devices, are still challenging for their industrial applications. In addition, a lack of knowledge about relevant and detailed mechanisms restricts the further development of electrocatalysts and devices. A timely review of the electrocatalysts, devices, and mechanisms is essential to shed lights on the correct direction towards further development. In this review, the advances in the design of electrocatalysts, fabrication of devices, and understanding of reaction mechanisms are comprehensively summarized and analyzed. The major challenges are also discussed as well as the potential approaches to overcoming them. The insights for further development are provided to offer a sustainable and environmentally friendly approach to cogeneration of energy and chemicals production.

Keywords: Organic molecules; Value-added chemicals; Electrocatalytic conversion; Hydrogen production

1. Introduction

The electrochemical conversion of small organic molecules to cogenerate value-added chemicals and hydrogen/electricity is attracting extensive interests since it produces energy (either hydrogen energy or electricity) and value-added chemicals simultaneously in a reaction system^[1–3]. Through this mode, not only the energy but also the value-added chemicals can be produced through the electrolysis of earth's abundant resources or wastes^[4] such as alcohol^[5], 5-hydroxymethylfurfural(5-HMF)^[6,7], formaldehyde^[8], hydrazine^[9], urea^[10–13], methane^[14], ethane^[15,16], propane^[17,18], butane^[19] etc. Most importantly, the process is CO₂ emission free, thus offering a sustainable and ecologically sound approach for cogeneration of energy and chemicals production^[8,20].

For water splitting, it is well known that more than 80% of the electricity is consumed by the oxygen evolution reaction (OER) at the anode according to a thermodynamic analysis^[21]. The main reason is ascribed to the high theoretical potential of OER (1.23 V)^[22–24]. For the co-electrolysis, the hydrogen is generated at the cathode and the OER of the anode is replaced by the oxidation reaction of these small organic molecules, thereby breaking theoretical 1.23 V limit, and greatly reducing the reaction potential and realizing hydrogen production with low energy consumption^[25]. Through such a reaction system, hydrogen and value-added chemicals can be produced simultaneously without CO₂ emission^[2,26].

In addition to the co-generation of hydrogen and value-added chemicals, it can also produce electricity and value-added chemical simultaneously. The most direct way is to build a fuel cell system using small organic molecules as fuel to directly generate electricity and value-added chemicals. It converts directly into electricity using the energy released by small organic molecules during the oxidation process. For instance, using alkanes such as ethane as raw materials, based on the solid oxidation fuel cell

system, it is possible to simultaneously generate electricity and co-produce the value-added chemical ethylene^[15,16,27], which provides a brand-new way to utilize alkane conversion without CO₂ emission.

These electrochemical methods have shown promise in selectively converting^[28] small organic molecules to hydrogen/electricity and other valuable products, without generating CO₂ as a byproduct^[29]. Electrocatalysts, the materials that facilitate electrochemical reactions, have been designed and optimized for efficient conversion of small organic molecules, enabling high selectivity and conversion efficiency. The progress has been promising, with the advancements in electrocatalysis, reactor design, and mechanistic understanding.

Despite the progress made, challenges remain, including catalyst stability, scale-up, cost, and regulatory considerations. Further research and development efforts in reactor design, electrode architectures, and mass transport management are needed to enhance the conversion efficiency, selectivity, and stability of the electrochemical processes. Process optimization approaches, such as control of electrode potential, temperature, and flow rates, are also necessary to achieve efficient and sustainable operation of electrochemical systems. The progress in recent years has shown promising potential, having offered a sustainable and ecologically sound approach for cogeneration of energy and chemicals production.

In this review, the advances are summarized and analyzed for the electrochemical conversion of small organic molecules to cogenerate hydrogen/electricity and value-added chemicals without CO₂ emission, as shown in Fig. 1. The small organic molecules which are candidates for the electrochemical conversion are first introduced, and then the recent advances in the development of electrocatalysts, devices and reaction mechanisms are reviewed. Finally, the major challenges and potential future

approaches are discussed. The insights into further development are provided from the perspective of both fundamental understanding and technological applications in the future.

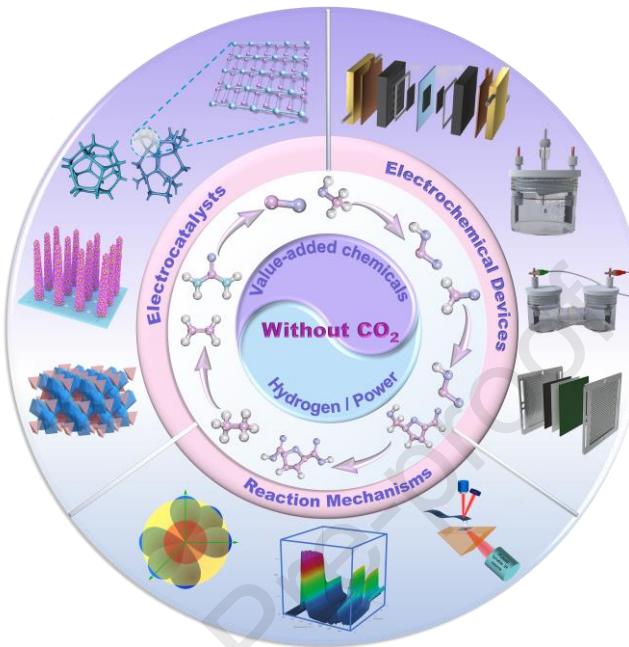


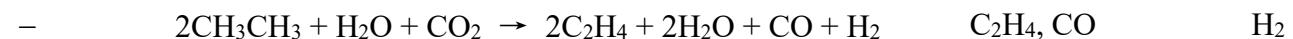
Fig. 1. Illustration of the conversion of small organic molecules to hydrogen/electricity and value-added chemicals without CO₂ emission by electrochemical conversion.

2. Feedstock of small organic molecules for electrochemical conversion

There are various feedstocks for small organic molecules for electrochemical conversion to hydrogen/electricity and value-added chemicals without CO₂ emission [30–33]. Table 1 lists the small organic molecules that are frequently used for electrochemical conversion to produce electricity/H₂, along with their bond energies, oxidation potentials, and overall reactions. They primarily consist of the following four categories: wastewater treatment, alkane conversion, alcohol conversion, and biomass conversion.

Table 1. Bond energies (in kJ mol^{-1}), standard potentials (V versus standard hydrogen electrode (SHE)) of typical small organic molecules for electrochemical conversion to produce electricity/ H_2 .

Organic molecules	Bond energies ^[34] (kJ mol^{-1})	Standard Potentials (V vs SHE)	Total Reactions	Value-added products	Electricity/ H_2
H_2O	O–H: 498.7	1.23 V	$2\text{H}_2\text{O} \rightarrow 2\text{H}_2 \uparrow + \text{O}_2 \uparrow$	–	H_2
$\text{CO}(\text{NH}_2)_2$	N–H: 464.4	0.37 V ^[35]	$\text{CO}(\text{NH}_2)_2 + \text{H}_2\text{O} \rightarrow \text{N}_2 \uparrow + \text{CO}_2 \uparrow + 3\text{H}_2 \uparrow$	–	H_2
$\text{NH}_2\text{–NH}_2$	N–H: 338.1	–0.84 V ^[36]	$\text{N}_2\text{H}_4 \rightarrow \text{N}_2 \uparrow + 2\text{H}_2 \uparrow$	–	H_2
CH_3OH	C–H _{methyl} : 401.9 O–H: 440.2	0.04 V ^[37]	$\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{HCOOH} + 2\text{H}_2 \uparrow$	HCOOH	H_2
$\text{CH}_3\text{CH}_2\text{OH}$	C–H _{methylene} : 396.6	0.05 V ^[38]	$\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + 2\text{H}_2 \uparrow$	CH ₃ COOH	H_2
HCHO	C–H (–CHO): 368.4	–0.22 V ^[39]	$4\text{HCHO} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{HCOOH} + 2\text{H}_2$	HCOOH	H_2 and Electricity
^a FF	C–H(–CHO): 378.7	0.01 V ^[40]	$4\text{FF} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{FA} + 2\text{H}_2$	FA	H_2 and Electricity
^b HMF	C–H(–CHO): –	0.06 V ^[41]	$4\text{HMF} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{HMFCFA} + 2\text{H}_2$	–	H_2 and Electricity
H_2O	O–H: 498.7	–	$\text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{H}_2 + \text{CO} + \text{O}_2$	CO	H_2
CH_4	C–H: 439.3	–	$2\text{CH}_4 + \text{O}_2 \rightarrow \text{C}_2\text{H}_4 + 2\text{H}_2\text{O}$	C_2H_4	Electricity
		–	$2\text{CH}_4 + \text{CO}_2 \rightarrow \text{C}_2\text{H}_4 + 2\text{H}_2\text{O} + \text{CO}$	$\text{C}_2\text{H}_4, \text{CO}$	–
		–	$2\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_4 + 2\text{H}_2\text{O} + \text{H}_2$	C_2H_4	H_2
		–	$2\text{CH}_4 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{C}_2\text{H}_4 + 2\text{H}_2\text{O} + \text{CO} + \text{H}_2$	$\text{C}_2\text{H}_4, \text{CO}$	H_2
CH_3CH_3	C–H _{methyl} : 420.5	–	$2\text{CH}_3\text{CH}_3 + \text{O}_2 \rightarrow 2\text{C}_2\text{H}_4 + 2\text{H}_2\text{O}$	C_2H_4	Electricity
		–	$\text{CH}_3\text{CH}_3 + \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O} + \text{H}_2$	C_2H_4	H_2
		–	$\text{CH}_3\text{CH}_3 + \text{CO}_2 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O} + \text{CO}$	$\text{C}_2\text{H}_4, \text{CO}$	–



^a FF: Furfural; FA: Furfural acid; ^b HMF: 5-Hydroxymethylfurfural; HMFCA: 5-hydroxymethyl-2-furancarboxylic acid

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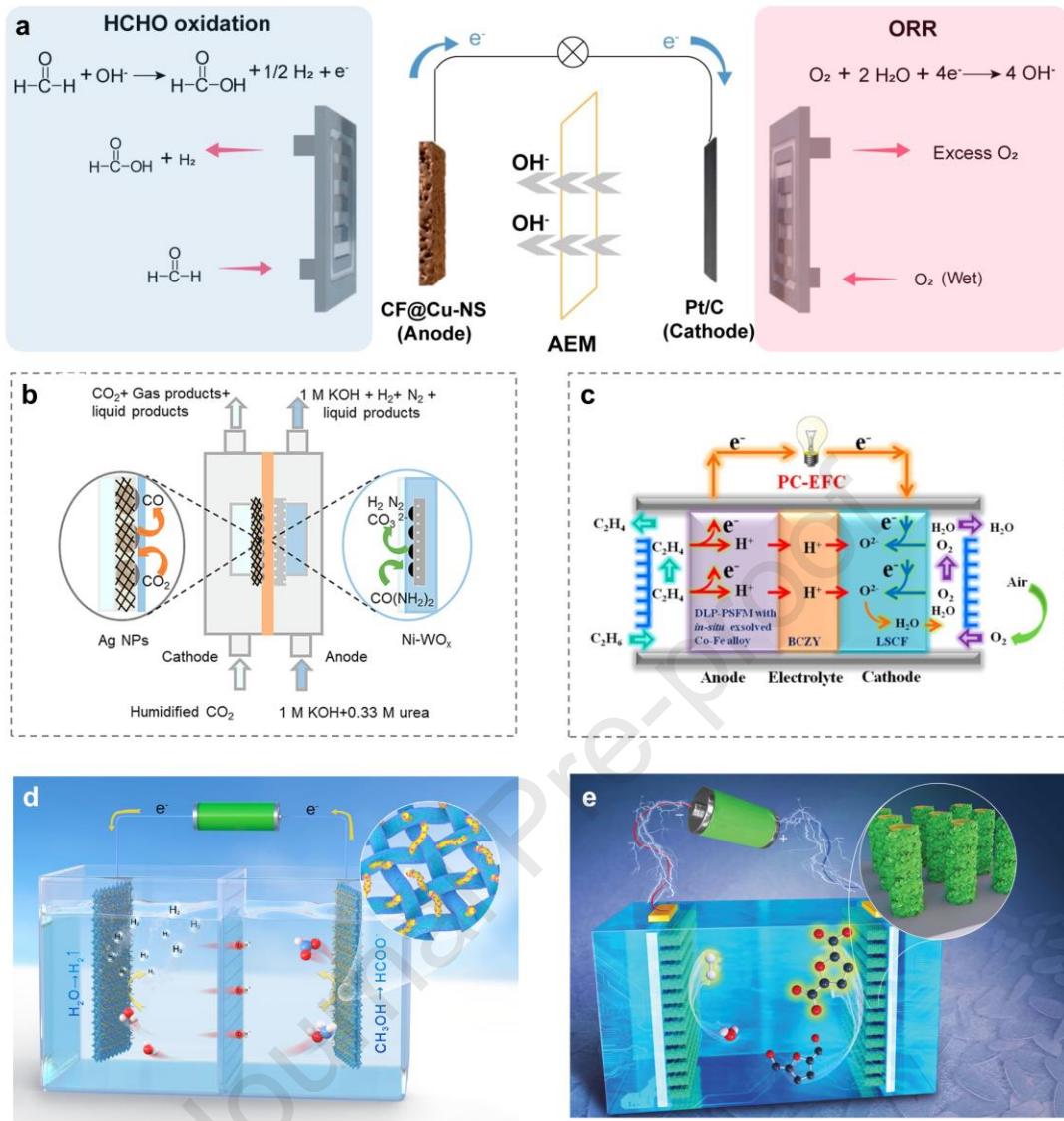


Fig. 2. Illustration of (a) Electricity, H₂ and formate cogeneration from formaldehyde fuel cell, (b) H₂ and CO cogeneration from the urea and CO₂ co-electrolysis. (c) Electricity and ethylene cogeneration from the selective oxidation of ethane by SOFC, (d) H₂ and formate cogeneration from the methanol and water co-electrolysis, (e) H₂ and HFDA cogeneration from the 5-HMF and water co-electrolysis, Reprinted from Ref.^[8] with permission from Wiley-VCH, Copyright 2023. Reprinted from Ref.^[10] with permission from Wiley-VCH, Copyright 2021. Reprinted from Ref.^[16] with permission from American Chemical Society, Copyright 2016. Reprinted from Ref.^[42] with permission from Elsevier, Copyright 2021. Reprinted from Ref.^[43] with permission

The most practical use of small organic molecules conversion is wastewater treatment^[44], such as elimination of formaldehyde^[8], urea^[45–48], hydrazine^[9] and etc. For instance, Yang et al.^[8] built a direct formaldehyde fuel cell out of formaldehyde and water, as illustrated in Fig. 2a. In this reaction, formaldehyde is selectively oxidized into formic acid, yielding both hydrogen and electricity. The reaction has a selectivity of greater than 99% and a Faradaic efficiency of 200%. This process not only removes formaldehyde but also delivers energies (electricity and hydrogen) and value-added chemical formate, thus killing three birds with one stone. The co-electrolysis of urea and water is a comparable process^[10] as illustrated in Fig. 2b. By combining the cathode CO₂ reduction process with the co-electrolysis of anode urea and water, both hydrogen and value-added chemical CO can be produced.

Alkanes, such as methane^[14], ethane^[15,16], propane^[17,18], butane^[19] etc., are the second most prominent small organic molecules as feedstocks, which can produce value-added alkenes. Because the activation of alkane normally necessitates the activation of C–H bonds, it is exceedingly difficult at low-temperature. As a result, high-temperature solid oxide fuel cells (SOFC) or solid oxide electrolytic cells (SOEC) are typically used. Ethane, as illustrated in Fig. 2c^[16], activates the C–H bonds in it via the catalyst, then conducts protons from the anode to the cathode via the proton conductor and combines with the oxygen in it to form water, turning chemical energy into electricity. At the same time, ethylene is produced by selective oxidation of ethane. Thus, electricity and the value-added chemical ethylene are generated simultaneously by such an electrochemical process.

The alcohols, such as methanol^[49–51] and ethanol^[5,52], are one of most prevalent small organic molecules as conversion feedstocks since they are widely produced. As

seen in Fig. 2d, methanol and water are co-electrolyzed [42], and the methanol is selectively oxidized at the anode to produce a value-added chemical formate that replaces the OER process. Hydrogen is produced at the cathode. Because the OER reaction at the anode is replaced by selective methanol oxidation reaction (MOR), the total energy consumption for the reaction is considerably decreased, resulting in low-energy hydrogen generation. Furthermore, the selectivity of value-added chemistry in this low-energy hydrogen generation process is as high as at 99%, and the Faradaic efficiency can exceed 95%. A process like this not only can produce hydrogen, but also value-added compounds like formate or acetate. Since methanol and ethanol are abundantly accessible, industry may develop such a cogeneration reaction system in the future to manufacture value-added chemicals while producing hydrogen at the same time.

Another popular feedstock is biomass^[53], the examples as furfural^[54], 5-HMF^[55,56], glycerol^[57] and etc. Typically, biomass is derived from trees, crop straw, and domestic garbage. Owing to its multiple advantages, i.e. great availability of diverse bioresources, ecofriendliness, and low cost, biomass resources have been used to produce a great range of biofuels and commercial chemicals all over the world. As seen in Fig. 2e^[43], 5-HMF may be selectively oxidized to HFDA at the anode, substituting the OER process and significantly lowering the reaction potential. Hydrogen is also generated at the cathode. Because the anode's OER reaction is substituted by the selective oxygen reaction of 5-HMF, low energy hydrogen generation is achieved. Since biomass is abundant and accessible in nature, it is possible to accomplish organic electrosynthesis and hydrogen generation by establishing such a cogeneration system.

3. Electrocatalysts

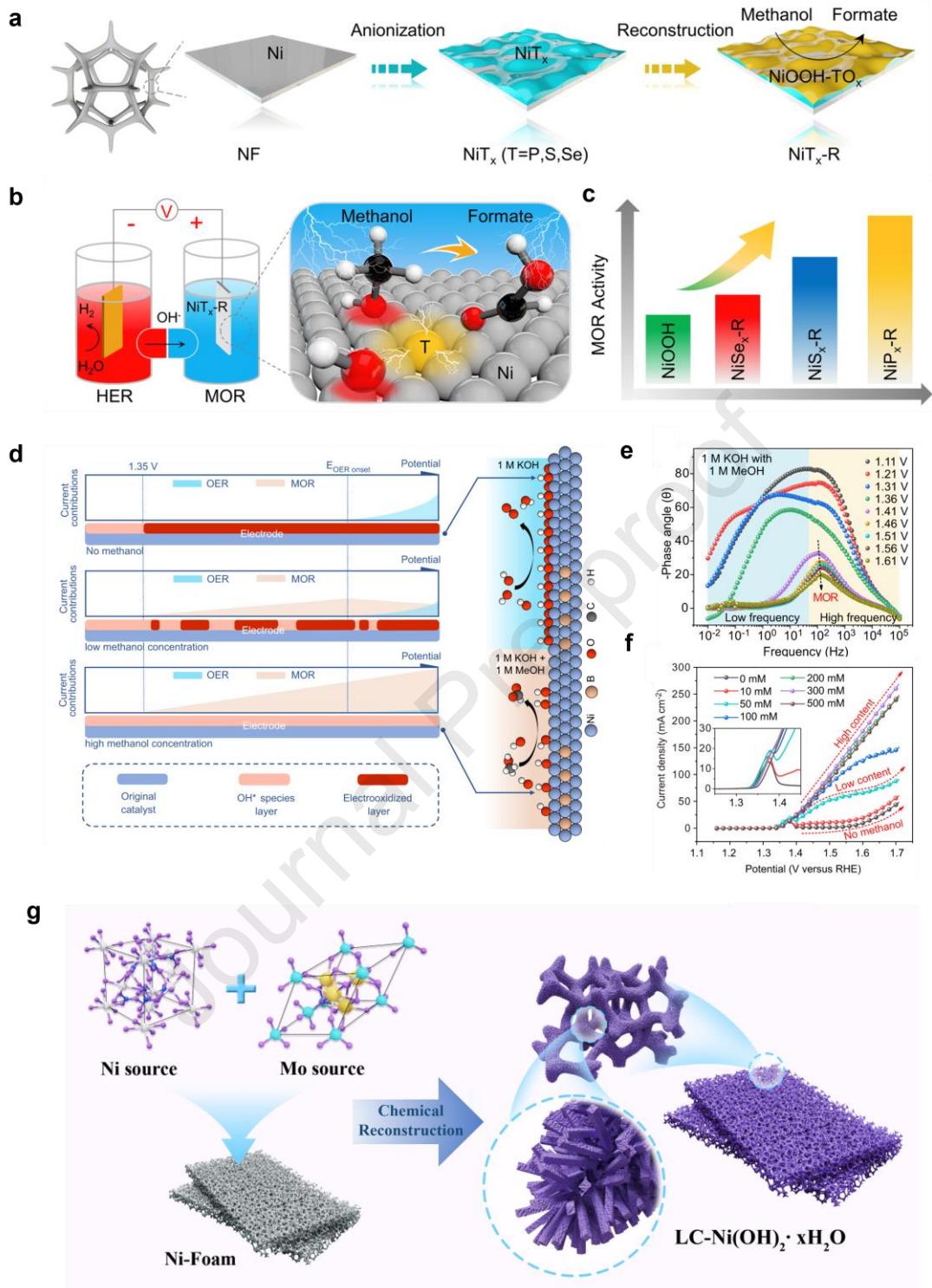


Fig. 3 (a) Illustration of the synthesis route of doped $\text{NiT}_x\text{-R}$ electrocatalysts^[58]. (b) An illustration showing the MOR process in relation to an H-type electrolytic cell^[58]. (c) MOR activity comparison of pure NiOOH , $\text{NiP}_x\text{-R}$, $\text{NiS}_x\text{-R}$, and $\text{NiSe}_x\text{-R}$ ^[58]. (d) Illustration of the MOR on NiB/Ni and the evolution of the catalyst. (e) Bode plots. (f) Linear Sweep Voltammetry (LSV) curves in electrolytes with different concentrations of methanol^[59]. (g) Illustration of chemical reconstruction of NiMoO_4 .

to form low coordinated Ni(OH)₂ [50].

The necessity for an effective catalyst is critical for achieving electricity generation from organic small molecules/low energy consumption hydrogen production and co-production of value-added chemicals^[1,60]. Such catalysts must have multiple merits of being inexpensive, and having excellent catalytic activity, stability, and selectivity^[61]. At present, the best catalysts for these reactions are noble metals such as Pt and their derivatives^[62,63]. However, due to the scarcity of noble metals, a variety of non-noble metals are being investigated as replacements to these noble metals, including nickel-based, perovskite-based, spinel-based catalysts etc. Here, the co-electrolysis systems of methanol/water and 5-HMF/water are taken as the examples to illustrate the development process of the electrocatalysts.

Non-noble Ni-based electrocatalysts including hydroxides^[20,50,64], oxyhydroxides^[58], oxides^[65], sulfides^[42], selenides^[51,66,67], boride^[59], carbide^[49] etc. are the most often employed for methanol/water co-electrolysis. To maximize the methanol electro-oxidation activity, Li et al. [58] investigated the coordination environment effect and discovered that it is crucial to control the nickel sites utilizing in-situ construction of various oxyanion-coordinated amorphous nickel oxyhydroxides (Fig. 3a). According to experimental and theoretical studies, NiOOH-PO_x improves OH* and methanol adsorption ability and promotes the production of CH₃O* intermediates (Fig. 3b). The coordinated phosphate oxygen-containing anion efficiently modifies the Ni site's *d*-band center and raises the Ni–O covalency, boosting catalytic activity (Fig. 3c). Further study into the activity of electrocatalyst for efficient methanol electrooxidation found

that the construction of heterostructure is an efficient way to enhance the performance of electrocatalysts^[25,59]. In-situ Raman and operando electrochemical impedance spectroscopies were employed to study the influence of methanol concentration on the MOR process. ^[59] It is found that the high methanol concentrations hinder the electrocatalyst's phase transition to high-valent electrooxidation products because the electrophilic active species, oxygen species (O^* or OH^*) form on the electrocatalyst (Figs. 3d and f). Further mechanistic investigations based on density functional theory (DFT) modeling show that the potential-determining step (*CH₂O production) is more likely to occur on heterostructures than on its single component compound, indicating that the construction of heterostructures is an efficient way to modulate the catalytic performance. Chemical reconstruction, in addition to generating heterojunctions, is a useful technique to increase the activity of Ni-based electrocatalysts. Fu et al. ^[50], for example, used chemical reconstruction to remove Mo from NiMoO₄, resulting in a low-coordinated Ni(OH)₂ (Fig. 3g). The low coordinated Ni(OH)₂ exhibits excellent activity and high stability because of its low-coordinated Ni–Ni configuration, three-dimensional network structure, and Mo dopant. In addition, a number of strategies have been used to improve the activity and durability of electrocatalysts by increasing the intrinsic activity, increasing active site density, or enhancing the electronic conductivity, such as dopant^[68], anode–cathode exchange^[69], spin modulation^[70], coordination effect^[58] etc. Metal serves as the primary catalytic active center in these metal-based electrocatalysts. For Ni-based electrocatalysts, for example, electrocatalysis is accomplished by the recycling of Ni^{2+}/Ni^{3+} .

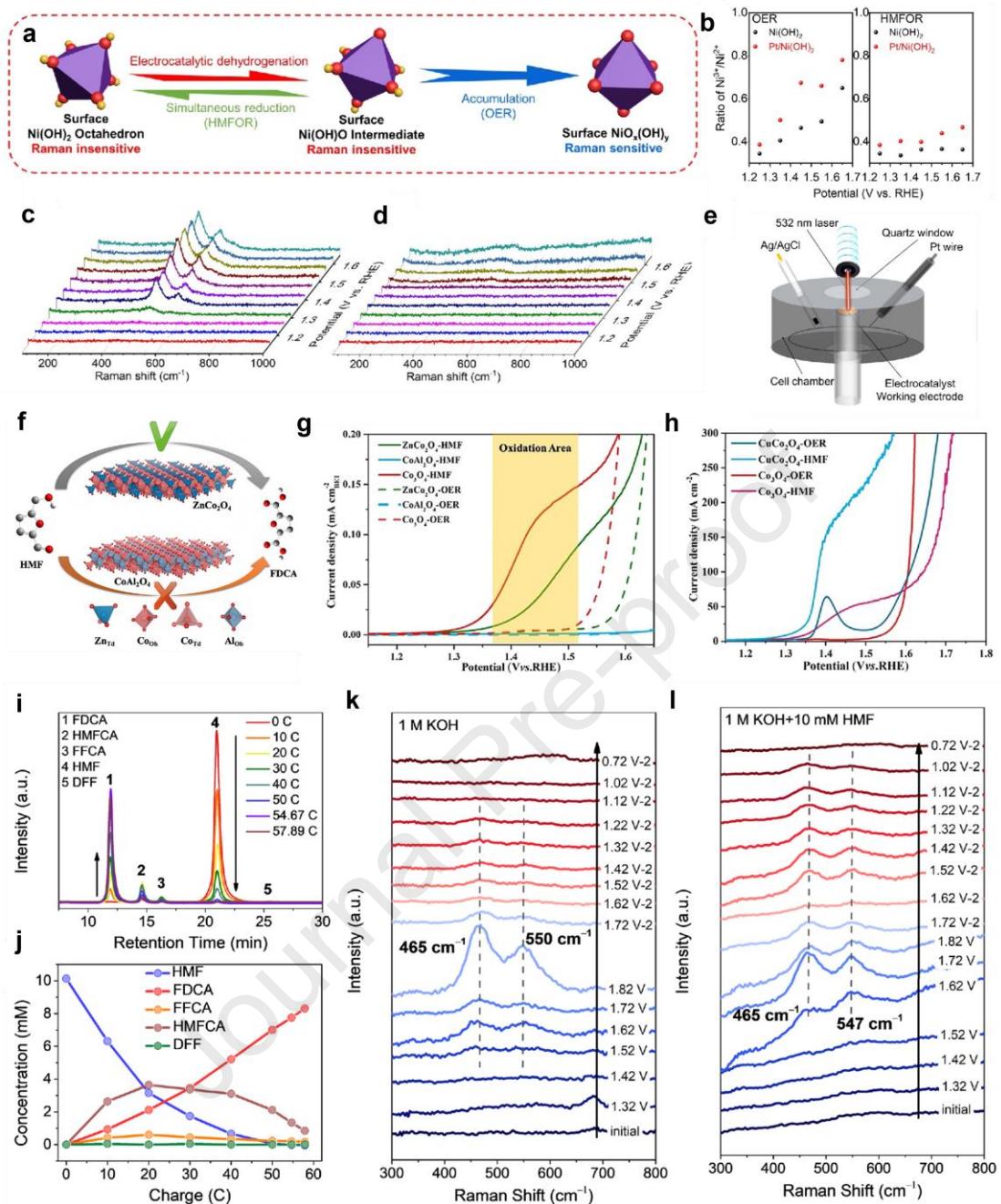


Fig. 4. (a) Illustration of transformation among $\text{Ni}(\text{OH})_2$, $\text{Ni}(\text{OH})\text{O}$, and $\text{NiO}_x(\text{OH})_y$ crystal structure. (b) The potential effect of the of $\text{Ni}^{3+}/\text{Ni}^{2+}$ ratio for HMFOR and OER processes. (c) The Raman spectroscopy for OER process. (d) The Raman spectroscopy for HMFOR process. (e) Illustration of Raman measurement during electrochemical process. Reprinted from Ref. [71] with permission from Wiley-VCH, Copyright 2021. (f) Illustrations for the electrocatalytic HMF oxidation by tetrahedron Zn^{2+} or octahedron Al^{3+} of spinel oxides. (g) LSV curves of ZnCo_2O_4 , Co_3O_4 , and CoAl_2O_4 normalized by BET area. (h) The electrochemical performance comparison for $\text{CuCo}_2\text{O}_4/\text{Ni}$ and $\text{CuCo}_2\text{O}_4/\text{OER}$. (i) HPLC chromatogram showing peaks 1, 2, 3, 4, and 5. (j) Concentration vs. Charge plot for HMF, FDCA, FFFCA, HMCA, and DFF. (k) Raman spectra of 1 M KOH at various potentials. (l) Raman spectra of 1 M KOH + 10 mM HMF at various potentials.

Co₃O₄/Ni. Reprinted from Ref.^[72] with permission from Wiley-VCH, Copyright 2020.

(i) High performance liquid chromatography (HPLC) traces for HMF and its oxidation products; (j) Charge effect for the concentration of HMF and its oxidation products. (k) In-situ Raman spectra in 1 M KOH; (l) In-situ Raman spectra in 1 M KOH + 10 mM HMF. Reprinted from Ref.^[73] with permission from Elsevier, Copyright 2022.

Similar to the methanol/water co-electrolysis, the nickel-based catalyst is also one of the most significant catalysts for the 5-HMF/H₂O co-electrolysis, such as Ni_xB^[74], Ru₁-NiO^[75], NiOOH^[76] etc. However, because the structures of 5-HMF and methanol differ, the catalyst has the unique properties that allow additional chemical modification to increase the selectivity of the 5-HMF's oxidation products. The most popular nickel-based electrocatalyst, Ni(OH)₂, not only has various catalytic effects on methanol/water system but also has a good catalytic effect on 5-HMF/H₂O system. In the case of Pt modulation, the redox characteristics of Ni(OH)₂ can be regulated, and the electrocatalytic activity can thus be increased^[71]. When compared to the Ni(OH)₂ electrode, the current density increases 8.2 times at the Pt/Ni(OH)₂ electrode. The Raman spectroscopies exhibit that the introduction of Pt improves the redox property of Ni(OH)₂ and speeds up the production of active center Ni(OH)O during the catalytic process (Fig. 4a). The appearance of NiO_x(OH)_y in the OER system causes the ratio of Ni³⁺/Ni²⁺ to increase rapidly in the potential range of 1.2 to 1.7 V. In contrast, the ratio of Ni³⁺/Ni²⁺ in the HMFOR system remains nearly constant before 1.55 V, which is consistent with the phenomenon of nucleophile oxidation reaction (Fig. 4b). The phase transition between Ni(OH)₂ and Ni(OH)O at the Ni(OH)₂ electrode was found in operando Raman spectra. In the context of the OER process, Ni(OH)₂ dehydrogenates

to generate Ni(OH)O, which then accumulates to form $\text{NiO}_x(\text{OH})_y$ after 1.35 V. The $\text{NiO}_x(\text{OH})_y$ can be detected in the operando Raman spectra (Figs. 4c and d), where the peaks at 473 and 553 cm^{-1} represent the bending and stretching vibrations of $\text{Ni}^{3+}-\text{O}$, respectively. In addition, the cobalt-based catalyst is also one of the most significant catalysts for the 5-HMF/water co-electrolysis^[77]. Lu et al.^[72] investigated the geometric site dependency of cobalt-based spinel oxides Co_3O_4 , ZnCo_2O_4 , and CoAl_2O_4 for the electrooxidation of 5-HMF (Fig. 4f). Tetrahedral Co^{2+} in Co_3O_4 is discovered to be capable of chemical adsorption for acidic organic compounds, while octahedral Co^{3+} plays a critical role in 5-HMF oxidation. Thus, changing the Lewis acidic site (the Co^{2+} site) and enhancing the exposure of Co^{3+} is a possible way to enhance the electrocatalytic performance of 5-HMF oxidation. As a typical example, Cu^{2+} can be used to substitute Co^{2+} in spinel oxides, increasing the degree of Co^{3+} exposure and acidic adsorption, hence greatly increasing the electrocatalytic activity for HMF electrooxidation. In addition, the study discovered that the dual effect from different metals can improve electrocatalytic efficiency^[73]. Song et al.^[73] developed the bifunctional electrode material NiCoP through the amalgamation of Ni-based electrocatalysts with metallic Co and non-metallic P. According to in-situ electrochemical impedance spectroscopy and Raman spectra (Figs. 4i–l), the CoNiP electrocatalyst experiences surface oxidation of metals followed by partial reduction by 5-HMF. Thus, the CoNiP electrocatalyst has increased electrical conductivity and moderates 2,5-furandicarboxylic acid (FDCA) desorption, resulting in improved catalytic activity.

For SOFC, the most frequently used electrocatalysts are non-noble based catalysts such as Ni-based ceramics, perovskites^[78,79], etc. Ni-based electrocatalyst have good performance for SOFC^[80]. However, when hydrocarbons are used as fuels, Ni-based anodes will catalytically break the C–H bonds, once the active sites of Ni are covered by coke, the consequence is the reduced activity and lack of long-term stability^[81]. Perovskite materials have mixed ionic conductivity and electronic conductivity, high catalytic activity for redox reactions, and good resistance to sulfur and carbon deposition to improve catalytic activity and stability^[82]. However, its catalytic activity and structural stability towards fuel gases are lower than those of metal catalysts. The main reason is the difference in its primary active sites. Metal Ni makes up most of the active centers in Ni-based electrocatalysts. However, oxygen vacancies account for the majority of the electrocatalytic active centers in perovskite electrocatalysts. In-situ precipitation of metal/alloy catalysts is an effective strategy to modify perovskite materials to improve electrocatalytic activity^[83]. In addition, the precipitated metal nanoparticles have a strong metal-oxide interface effect with the matrix, thereby limiting the agglomeration of metal nanoparticles, which can effectively avoid growth and agglomeration problems during long-term operation^[84]. Although some progress has been made in the research of electrocatalytic materials for high-temperature SOFC, the issue of long-term operation stability is still a hot research topic and requires further exploration and optimization.

Collectively, noble metals are often more electrocatalytically active and stable for the electrochemical conversion of small organic molecules. Due to their high cost and

scarcity, it has to be cost effective by reducing their usage as much as feasible while reasonably maintaining high activity and stability. Alternatively, the use of non-noble metals to replace the noble metals is a more promising solution. However, the operating voltage of the reaction is often higher for non-noble metals than for noble metals. Therefore, it is essential to design novel non-noble metal electrocatalysts that they preserve their stability and activity simultaneously at reduced working potential.

4. Devices

The advancement of electrochemical conversion of organic compounds has also been aided by reactor design and process optimization. To increase the conversion of small organic molecules to hydrogen and value-added chemicals, electrochemical reactors with enhanced mass transfer and energy efficiency have been constructed^[26]. Flow cells^[85], membrane reactors^[86], and electrode designs^[87] have been investigated as reactor topologies to improve reaction conditions and boost overall process efficiency.

The cathode and anode designs are unique for the reaction of biomass conversion, such as Cu-catalyzed 5-HMF cathode and anode to concurrently produce hydrogen^[4]. Both sides contain electrolyte inlets and outlets, as indicated in Fig. 5a. The oxidation process of the aldehyde group ($\text{R}-\text{CHO} + \text{OH}^- \rightarrow \text{R}-\text{COOH} + 1/2 \text{ H}_2 + \text{e}^-$) takes place at the anode. The water decomposition process for hydrogen evolution ($\text{H}_2\text{O} + \text{e}^- \rightarrow 1/2 \text{ H}_2 + \text{OH}^-$) occurs at the cathode. Between the cathode and anode is a special membrane that can transfer OH^- . Combining electrochemical systems with renewable energy sources (such as sunlight or wind) and energy storage technologies (such as batteries or supercapacitors) can provide a carbon-free and abundant source of electricity that can be used for driving electrochemical processes. Chen et al. [88]

integrated a solar-driven reaction using the photovoltaic electrocatalysis (PVEC) of BHMF for the co-production of FDCA and H₂ as shown in Figs. 5b and c. A complete conversion of 5-HMF to FDCA was achieved with over 90% yield and faradaic efficiency (FE). As seen in Fig. 5d, Houke et al. ^[89] constructed a MEA-type cell using dioxide materials with linear serpentine flow fields. For the anode, the modified Ni-based layer double hydroxide (Ni-LDH) was used, while the cathode, loading 0.1 mg Pt cm⁻², was coated using a spray approach. With such a setup, they demonstrated a family of stable and active Ni-based catalysts which works in a zero-gap MEA-type single electrolyzer cell to selectively oxidize biomass (Figs. 5e and f). This biomass electrolysis apparatus is able to produce a biopolymer precursor at a level never possibly achieved and could have cost benefits from the perspective of technology.

In light of the comparatively high reaction temperature of SOFC/SOEC systems carrying out the alkane conversion reactions, the device structure differs dramatically from that of a low-temperature electrolytic cell. The most notable distinction is that the anode and cathode electrodes and electrolytes are calcined into one body at high temperatures^[90], as shown in Fig. 6a. For the selective production of ethylene from ethane, the input gas ethane flows via a fixed bed onto the surface of the electrocatalyst to be oxidized to ethylene by proton conductor dehydrogenation, as indicated in Fig. 6b ^[14]. On the surface of the electrocatalyst, the reaction C₂H₆ → C₂H₄ + H⁺ + 2e⁻ occurs, producing protons. Subsequently, the electrolyte transports protons to the cathode, where they react with oxygen to produce H₂O (1/2 O₂ + 2H⁺ + 2e⁻ → 1/2 H₂O). The electrocatalytic device for oxygen ion conductors is similar to that for proton conductors ^[91]. The distinction is that H₂O or CO₂ forms oxygen ions at the cathode, which are brought to the anode via the solid electrolyte and combine with the alkanes to produce value-added chemicals and water.

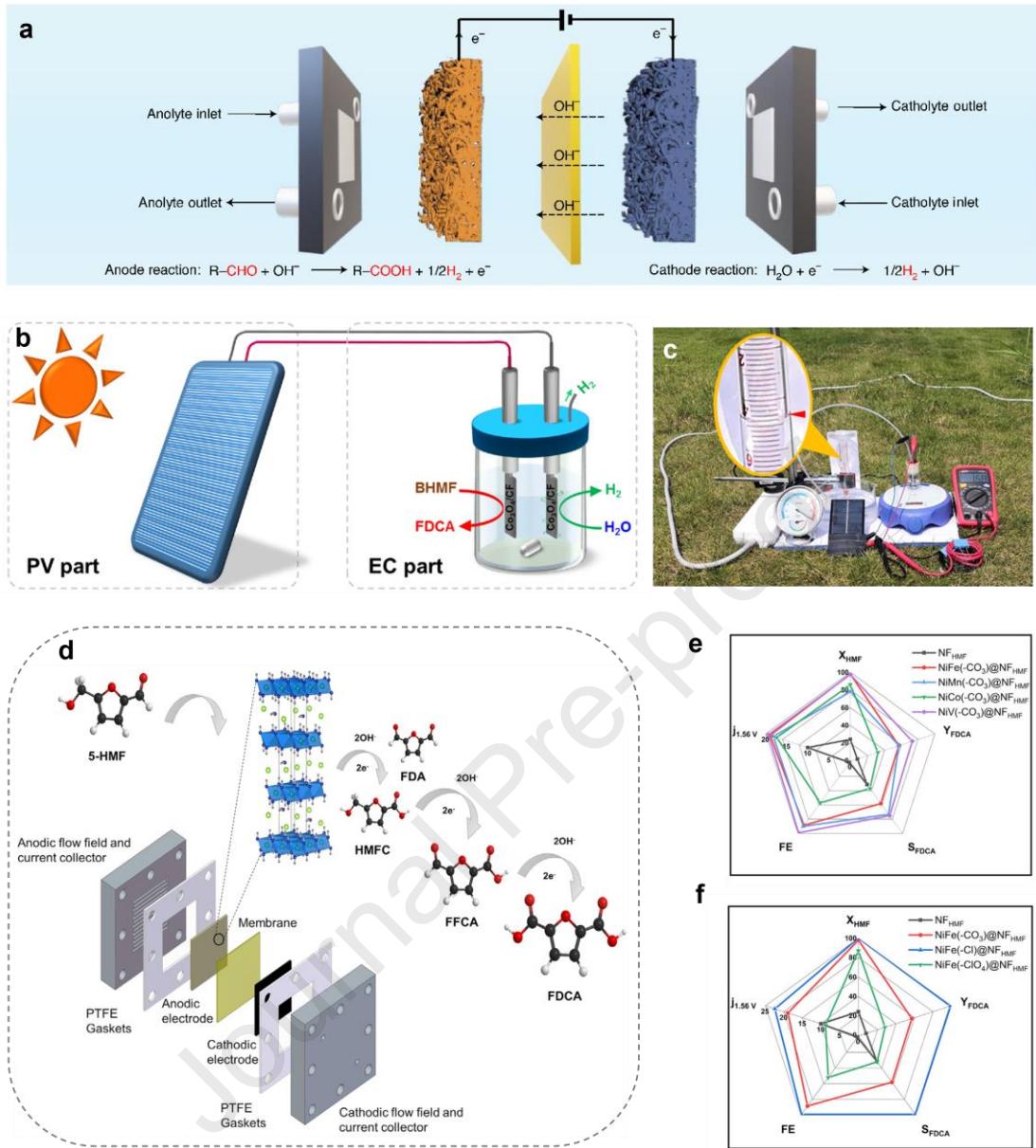


Fig. 5. (a) Illustration of a two-electrode electrolyzer that uses HER as the cathode reaction and aldehyde oxidation as the anode reaction. Reprinted from Ref.^[4] with permission from Springer Nature, Copyright 2021. (b) Illustration of PVEC for simultaneous BHMF oxidation and HER. (c) Image of natural sunlight irradiation. Reprinted from Ref.^[88] with permission from Elsevier, Copyright 2022. (d) Illustration of selective oxidation of biomass in an electrolyzer using Ni-based catalysts. The conversion (X), yield (Y), selectivity (S), and FE are given for $\text{NiX}(\text{-A}^-)\text{-LDH@NF}$ electrocatalysts on a scale of 0% ~ 100%, and the current density at $+1.56\text{ V}_{\text{cell}}$ is plotted in the range of $0 \sim 20\text{ mA cm}^{-2}$ in (e) and $0 \sim 25\text{ mA cm}^{-2}$ in (f). Reprinted from Ref [89].

The systems that co-produce value-added chemicals and hydrogen/electricity through electrocatalysis of small organic molecules such as alcohol do not have high device requirements. This is determined by the characteristics of these reaction systems. The products produced by the reaction systems are gas products and liquid products that can be easily separated. Obviously, this characteristic is a natural advantage in terms of large-scale industrial applications.

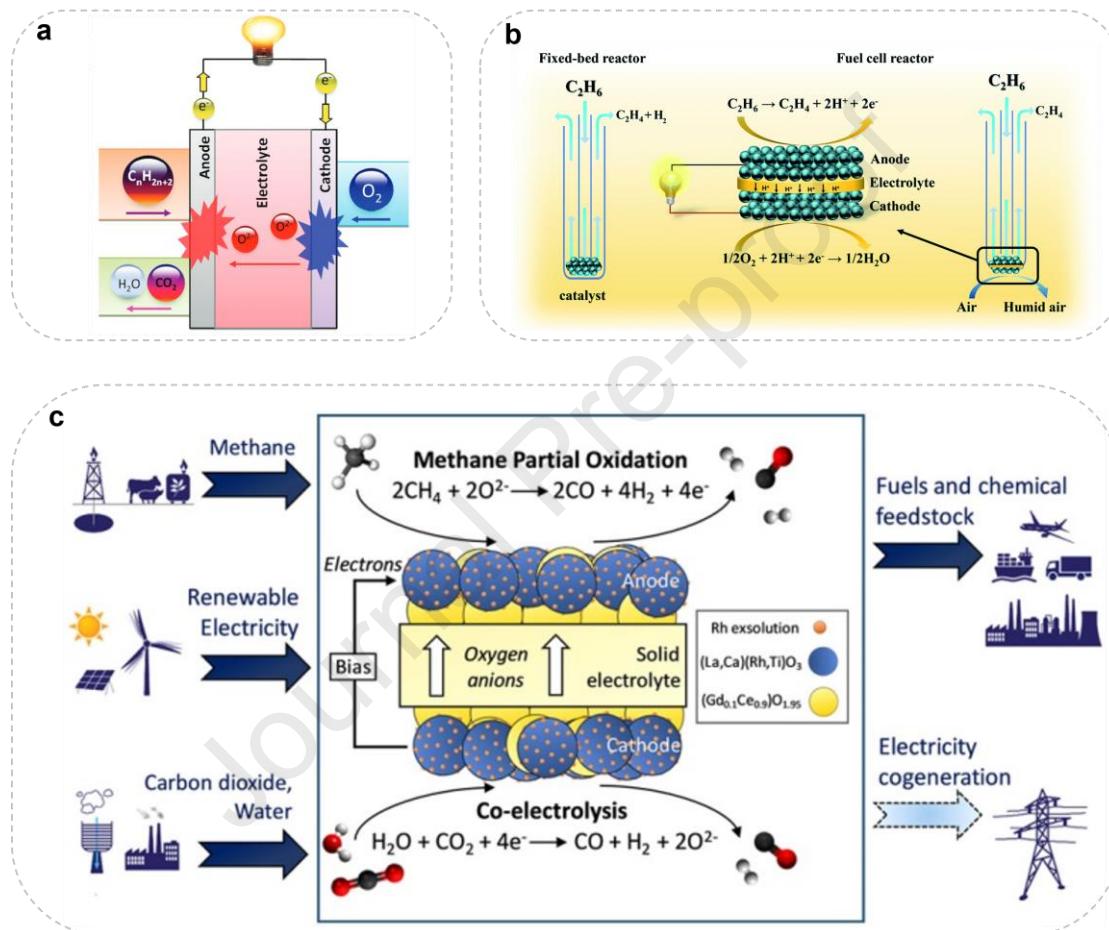


Fig. 6. (a) A schematic drawing of alkane fuel cells for cogeneration of electricity and valuable alkenes. Reprinted from Ref. [90] with permission from Royal Society of Chemistry, Copyright 2011. (b) Ethane dehydrogenation in a fixed-bed reactor and fuel cell reactor. Reprinted from Ref. [15] with permission from the Royal Society of Chemistry, Copyright 2020. (c) Illustration of cogeneration of electricity and value-added chemicals via syngas. Reprinted from Ref. [14] with permission from American Chemical Society, Copyright 2020.

Electrochemical water treatment systems are more sophisticated than value-

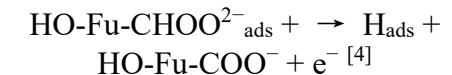
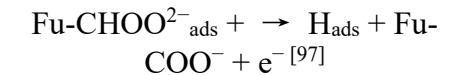
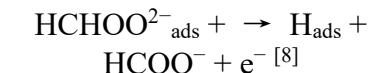
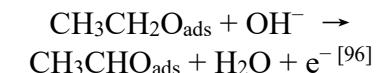
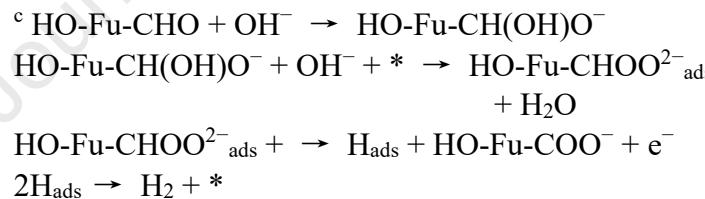
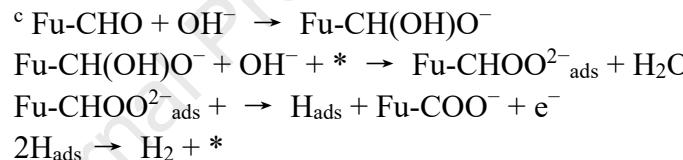
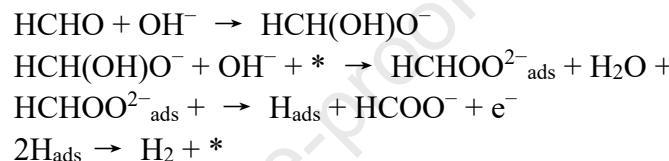
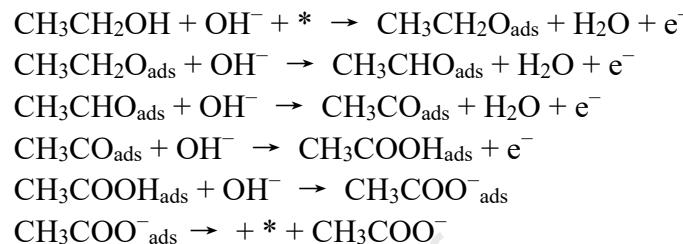
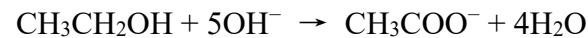
added chemical and hydrogen generation systems. Because water typically contains few pollutants, the mass transfer processes of pollutants from the electrolyte to the electrode surface reduce treatment efficiencies. Thus, the system design for electrochemical treatment is predominantly concerned with increasing electrode surface area and reaction time. Many electrochemical water treatment systems employ porous materials as current collectors to improve the electrode surface area and hence the rate of pollutant conversion. Developing an electrolyte recirculation system to increase the response time is another prosperous method that has been extensively adopted in the water treatment industry^[92].

5. Mechanisms

Understanding the reaction mechanisms and kinetics of electrochemical conversion of small organic molecules using techniques such as in-situ spectroscopy, electrochemical techniques, and computational modeling could provide insights into the fundamental aspects of the electrochemical conversion processes, allowing for improved catalyst design and reaction optimization. A number of detailed mechanistic studies have been performed for these small organic molecules^[5,42,93,94]. Here, the most possible reaction pathway and limit step for electrochemical conversion of small organic molecules for producing electricity/H₂ are listed in Table 2 and their merits and demerits are listed in Table 3.

Table 2. The most possible reaction pathways and limit steps of electrochemical conversion and associated electrochemical reactions for producing electricity/H₂.

Reactions	Most possible reaction pathway	Possible limit step
$\text{CO}(\text{NH}_2)_2 + 6\text{OH}^- \rightarrow \text{N}_2 + \text{CO}_2 + 5\text{H}_2\text{O} + 6\text{e}^-$	$\text{CO}(\text{NH}_2)_2 + \text{OH}^- + * \rightarrow \text{CO}(\text{NH}_2)(\text{NH})_{\text{ads}} + \text{H}_2\text{O} + \text{e}^-$ $\text{CO}(\text{NH}_2)_{2\text{ads}} + \text{OH}^- \rightarrow \text{CO}(\text{NH}_2)_{\text{ads}} + \text{H}_2\text{O} + \text{e}^-$ $\text{CO}(\text{NH}_2)_{2\text{ads}} + \text{OH}^- \rightarrow \text{CON}(\text{NH})_{\text{ads}} + \text{H}_2\text{O} + \text{e}^-$ $\text{CO}(\text{NH}_2)_{2\text{ads}} + \text{OH}^- \rightarrow \text{CON}_{2\text{ads}} + \text{H}_2\text{O} + \text{e}^-$ $\text{CON}_{2\text{ads}} + \text{OH}^- \rightarrow \text{CO}(\text{OH})\text{N}_{2\text{ads}} + \text{e}^-$ $\text{CO}(\text{OH})\text{N}_{2\text{ads}} + \text{OH}^- \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{N}_2 + * + \text{e}^-$	$\text{CO}(\text{NH}_2)_2 + \text{OH}^- + * \rightarrow \text{CO}(\text{NH}_2)(\text{NH})_{\text{ads}} + \text{H}_2\text{O} + \text{e}^-$ $\text{CO}(\text{NH}_2)(\text{NH})_{\text{ads}} + \text{H}_2\text{O} + \text{e}^-$ ^[12]
$\text{N}_2\text{H}_4 + 4\text{OH}^- \rightarrow \text{N}_2 + 4\text{H}_2\text{O} + 4\text{e}^-$	$\text{N}_2\text{H}_4 + \text{OH}^- + * \rightarrow \text{H}_2\text{NNH}_{\text{ads}} + \text{H}_2\text{O} + \text{e}^-$ $\text{H}_2\text{NNH}_{\text{ads}} + \text{OH}^- \rightarrow \text{HNNH}_{\text{ads}} + \text{H}_2\text{O} + \text{e}^-$ $\text{HNNH}_{\text{ads}} + \text{OH}^- \rightarrow \text{NNH}_{\text{ads}} + \text{H}_2\text{O} + \text{e}^-$ $\text{HNN}_{\text{ads}} + \text{OH}^- \rightarrow \text{N}_{2\text{ads}} + \text{H}_2\text{O} + \text{e}^-$ $\text{N}_{2\text{ads}} \rightarrow \text{N}_2 + *$	$\text{N}_2\text{H}_4 + \text{OH}^- + * \rightarrow \text{H}_2\text{NNH}_{\text{ads}} + \text{H}_2\text{O} + \text{e}^-$ $\text{H}_2\text{NNH}_{\text{ads}} + \text{H}_2\text{O} + \text{e}^-$ ^[95]
$\text{CH}_3\text{OH} + 5\text{OH}^- \rightarrow \text{HCOO}^- + 4\text{H}_2\text{O} + 4\text{e}^-$	$\text{CH}_3\text{OH} + \text{OH}^- + * \rightarrow \text{CH}_3\text{O}_{\text{ads}} + \text{H}_2\text{O} + \text{e}^-$ $\text{CH}_3\text{O}_{\text{ads}} + \text{OH}^- \rightarrow \text{CH}_2\text{O}_{\text{ads}} + \text{H}_2\text{O} + \text{e}^-$ $\text{CH}_2\text{O}_{\text{ads}} + \text{OH}^- \rightarrow \text{CHO}_{\text{ads}} + \text{H}_2\text{O} + \text{e}^-$ $\text{CHO}_{\text{ads}} + \text{OH}^- \rightarrow \text{HCOOH}_{\text{ads}} + \text{e}^-$ $\text{HCOOH}_{\text{ads}} + \text{OH}^- \rightarrow \text{HCOO}^-_{\text{ads}}$ $\text{HCOO}^-_{\text{ads}} \rightarrow + * + \text{HCOO}^-$	$\text{CH}_3\text{O}_{\text{ads}} + \text{OH}^- \rightarrow \text{CH}_2\text{O}_{\text{ads}} + \text{H}_2\text{O} + \text{e}^-$ ^[51]



^a FF: Furfural; FA: Furfural acid; ^b HMF: 5-Hydroxymethylfurfural; HMFC^a: 5-hydroxymethyl-2-furancarboxylic acid ^c Fu: furan ring

Table 3. Merits and demerits for electrochemical conversion and associated electrochemical reactions for producing electricity/H₂.

Reactions	Merits	Demerits
$\text{CO}(\text{NH}_2)_2 + 6\text{OH}^- \rightarrow \text{N}_2 + \text{CO}_2 + 5\text{H}_2\text{O} + 6\text{e}^-$	Low reaction potential (~1.3 V vs RHE)	Low value of the product (N ₂) CO ₂ emission
$\text{N}_2\text{H}_4 + 4\text{OH}^- \rightarrow \text{N}_2 + 4\text{H}_2\text{O} + 4\text{e}^-$	Ultra-low reaction potential (~0 V vs RHE)	Low value of the product (N ₂) Toxic feedstock (N ₂ H ₄)
$\text{CH}_3\text{OH} + 5\text{OH}^- \rightarrow \text{HCOO}^- + 4\text{H}_2\text{O} + 4\text{e}^-$	Low reaction potential (~1.3 V vs RHE) Valuable product (HCOO ⁻) CO ₂ emission free	
$\text{CH}_3\text{CH}_2\text{OH} + 5\text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + 4\text{H}_2\text{O}$	Low reaction potential (~1.3 V vs RHE) Valuable product (CH ₃ HCOO ⁻) CO ₂ emission free	
$2\text{HCHO} + 4\text{OH}^- \rightarrow 2\text{HCOO}^- + 2\text{H}_2\text{O} + \text{H}_2 + 2\text{e}^-$	Ultra-low reaction potential (~0 V vs RHE) Highly-valuable product (HCOO ⁻ and H ₂) CO ₂ emission free	Toxic feedstock (HCHO) Side reactions in electrolyte (Cannizaro reaction)
^a $4\text{FF} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{FA} + 2\text{H}_2$	Ultra-low reaction potential (~0.1 V vs RHE) Highly-valuable product (FA and H ₂) CO ₂ emission free Biomass feedstock (FF)	Fast decay of the catalyst activity Side reactions in electrolyte (Cannizaro reaction)
^b $4\text{HMF} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{HMFAC} + 2\text{H}_2$	Ultra-low reaction potential (~0.1 V vs RHE) Highly-valuable product (HMFCA and H ₂) CO ₂ emission free Biomass feedstock (HMF)	Fast decay of the catalyst activity Side reactions in electrolyte (Cannizaro reaction)

^a FF: Furfural; FA: Furfural acid; ^b HMF: 5-Hydroxymethylfurfural; HMFCA: 5-hydroxymethyl-2-furancarboxylic acid

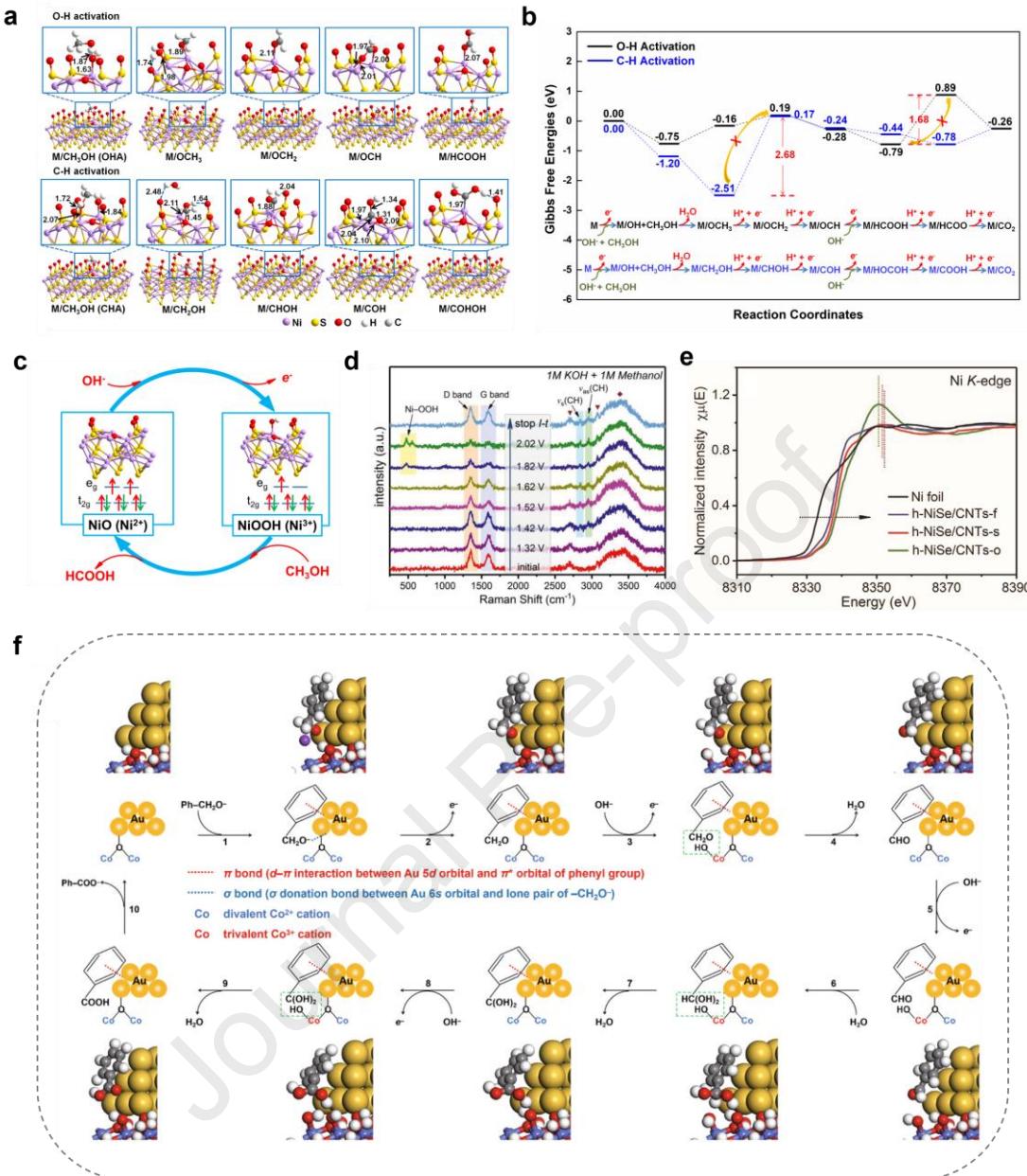


Fig. 7. (a) Intermediates of anodic selective oxidation of methanol of methanol/water co-electrocatalysis by Ni_3S_2 . (b) Energy profiles for methanol/water co-electrocatalysis by Ni_3S_2 (c) Redox cycle of $\text{Ni}^{3+}/\text{Ni}^{2+}$. Reprinted from Ref.^[42] with permission from Elsevier, Copyright 2021. (d) In-situ Raman for intermediates of NiOOH and intermediate $^*\text{CH}_2$ for the methanol/water co-electrocatalysis by NiSe (e) XANES spectra at Ni K-edge for NiSe . Reprinted from Ref.^[51] with permission from Wiley-VCH, Copyright 2020. (f) Illustrations of the reaction processes for benzyl alcohol oxidation catalyzed by Au/CoOOH ^[5].

As shown in Table 2, in the processes of co-electrolysis of $\text{CO}(\text{NH}_2)_2/\text{H}_2\text{O}$ and

$\text{N}_2\text{H}_4/\text{H}_2\text{O}$ systems, N–H activation has been reported to be the limit step. As a result, the catalyst's design for these reactions depends on how to activate the N–H bonds. They are also similar in that they are unable to generate value-added products. However, this is a wastewater treatment procedure, and the decontamination process provides a significant value to the process. For $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ and $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$ co-electrolysis, the limiting step is the second step, the activation of C–H. Therefore, designing high performance electrocatalysts for C–H activation is crucial for this type of reaction. The limiting step in the oxidations of formaldehyde, FF, and HMF in an alkaline environment is the dehydrogenation of divalent anions to monovalent anions. As a result, the design of catalysts should primarily consider this process.

To broaden the application scope of non-noble metal materials and increase their stability, Zhao et al. [42,51] investigated the effects of the surface evolution process of nickel-based materials on the electrocatalytic methanol/water co-electrolysis production of hydrogen reaction mechanism (Figs. 6a–e) using in-situ Raman spectroscopy in conjunction with DFT calculations. It has been discovered that the predominant active site for nickel-based materials is in-situ generated NiOOH. Oxidation, hydroxylation, reconstruction, and other surface evolution processes of nickel-based materials play significant roles in the formation of the electrocatalytic active center during the production of NiOOH (Fig. 6a). The substantial adsorption of the intermediate HCOO^* , which makes it challenging to continue oxidation to generate CO_2 , is the main factor underlying why methanol may be oxidized to HCOO^- with excellent selectivity (Fig. 6b). This oxidation of methanol is electrocatalyzed by nickel-based materials, and the $\text{Ni}^{3+}/\text{Ni}^{2+}$ oxidation–reduction cycle pair provides the oxidation driving force (Fig. 6c). These studies demonstrate that the evolution of the surface of non-noble metals plays a key role in determining their reactivity and that the process of surface evolution of non-noble metal materials presents a significant barrier

to their stability. Li et al. [5] showed high current density electrooxidation of benzyl alcohol combined with H₂ generation over a cooperative catalyst of Au supported on Au/CoOOH. In a two-electrode membrane-free flow electrolyzer, the absolute current may be increased to 4.8 A at 2.0 V. According to DFT studies, benzyl alcohol may be enhanced at the Au/CoOOH interface and oxidized by the electrophilic OH* produced on CoOOH, resulting in greater activity than pure Au. Through the establishment of heterostructures and the suppression of surface reconstruction, the addition of Au greatly improves the stability of the non-noble metal Co²⁺/Co³⁺. Based on the observation that the catalyst can be reversibly oxidized/reduced at anodic potential/open circuit, they developed a useful long-term alcohol electrooxidation method that reduces energy consumption and promotes productivity with a high current density (>250 mA cm⁻²) within 24 hours.

The process of electrocatalytically coupled biomass selective oxidation for producing hydrogen is substantially more complex due to the variety of biomass^[98]. Biomass, including cellulose and hemicellulose, could be transformed into fructose and xylose, as illustrated in Fig. 8a. Fructose can produce HMF and MMF, while xylose can produce furfural. FDCA may be produced by HMF, MMF, and furfural. These are the building blocks for a variety of polymers. Liu et al. ^[86] studied the oxidation process of furfural on the (111) surfaces of Pt, Cu, and Au (Fig. 8b) and discovered that Cu has a poorer adsorption of furfural oxidation reaction intermediates than Cu and Pt. This weakening of adsorption promotes product desorption, making Cu the most active of the three metals. According to additional studies, the diol route has become the most significant reaction pathway since it has the lowest energy barrier. Deng et al. ^[99] also investigated the mechanism of Co³⁺/Co⁴⁺ element conversion and discovered that the reaction kinetics of Co³⁺ oxidation and HMF oxidation are considerably lower than the

reaction kinetics of Co^{4+} , as shown in Fig. 8d.

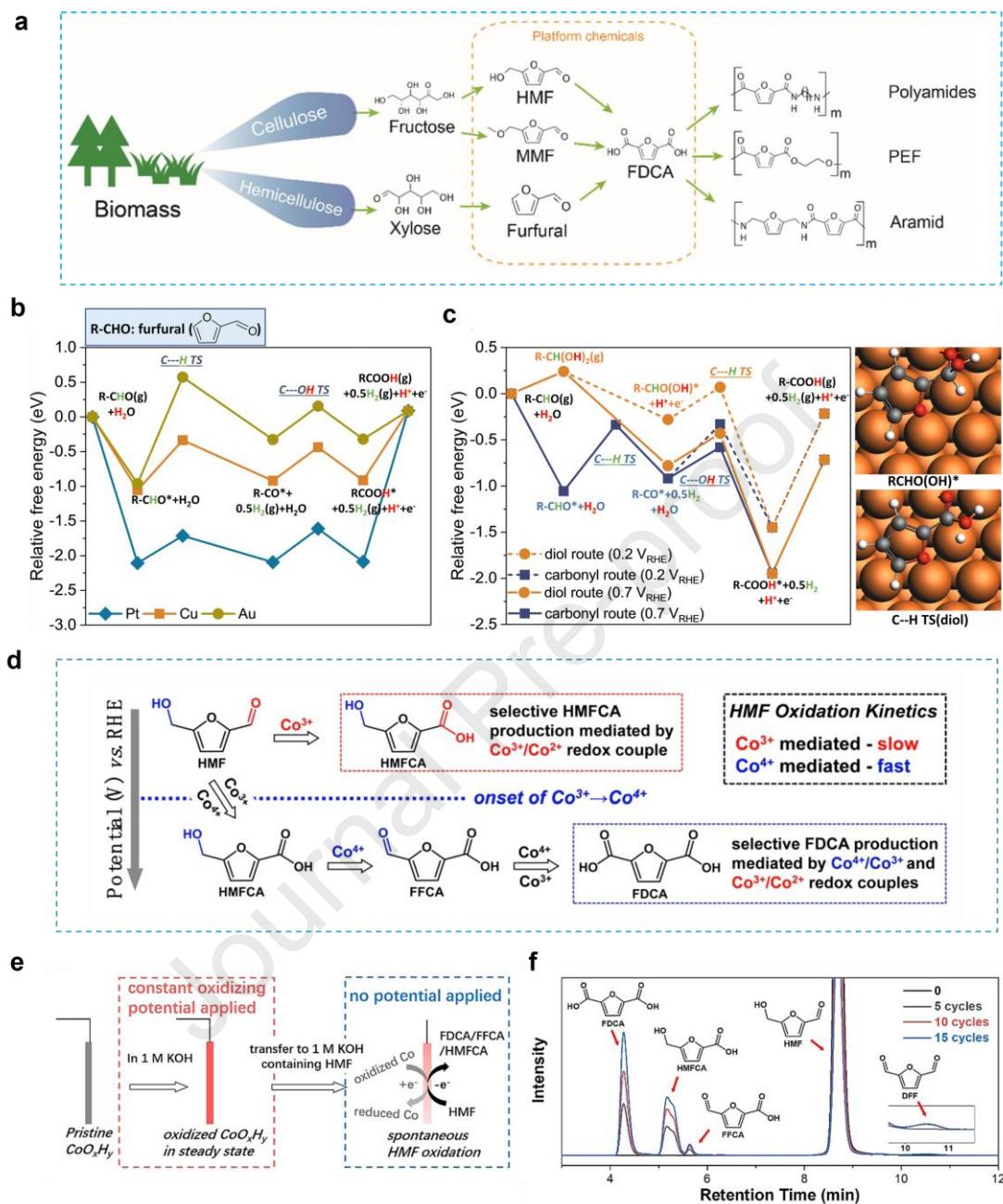


Fig. 8. (a) Illustration of the electrocatalytic conversion of biomass-derived furans into various value-added chemicals. Reprinted from Ref.^[94] with permission from Springer, Copyright 2020. (b) Comparison of the furfural oxidation on Pt(111)/Cu(111)/Au(111) surfaces. (c) Free energies diagram for carbonyl and diol routes on the Cu(111) surface and associated intermediate/transition state structures of the diol mechanism. Reprinted from Ref.^[86] with permission from the Royal Society of Chemistry, Copyright 2022. (d) Illustration of the potential-dependent oxidation of HMF to yield HMFCAs and FDCA

facilitating by the electrogenerated $\text{Co}^{3+}/\text{Co}^{4+}$. (e) The protocol to determine the function of Co^{4+} for the “Electrochemical–Chemical” pathway. (f) Traces from the HPLC chromatogram obtained after five, ten, and fifteen cycles. Reprinted from Ref.^[99] with permission from Wiley, Copyright 2021.

Although some progress has been made in understanding the electrocatalytic processes of these organic molecules, challenges remain. The main problem is that many chemical intermediates cannot be accurately detected. Most in-situ techniques are currently unable to adequately capture the chemical intermediates due to solvent interference. Common calculation techniques also overlook the solvation effect. As a result, in the future, more advanced in-situ spectroscopic techniques and computational approaches involving solvation need to be developed to capture reaction intermediates, revealing more detailed reaction mechanisms.

6. Challenges and perspectives

Although the research on the electrocatalytic co-generation of value-added chemicals and hydrogen/electricity systems of small organic molecules has made significant progress, there still exist many challenges involving reaction system selectivity and efficiency, catalyst activity and stability, mechanistic understanding, industrial reaction amplification, among other aspects.

First, achieving high selectivity and conversion efficiency for the desired products can be challenging due to the complex nature of organic feedstocks. Organic molecules often have multiple functional groups and can undergo various competing reactions, leading to a mixture of products. Controlling the electrochemical reactions to produce the desired products while minimizing unwanted side reactions can be difficult. Developing highly active and selective electrocatalysts for specific organic molecules

is a key challenge. Controlling the reaction selectivity to obtain the desired products while minimizing unwanted by-products can be challenging and requires precise control of reaction conditions, electrode potentials, and catalyst properties. In co-electrolysis systems involving organic molecule and water, such as methanol/water, formaldehyde/water, 5-HMF/water, and others, the selectivity of the conversion can be enhanced by accurately controlling the potential and the adsorption/ energy of catalysts for reactants (especially for reaction intermediate). It is possible to regulate the potential of these systems in order to get a product selectivity of greater than 95% or even 99%. However, because the temperature in high-temperature SOFC/SOEC is more than 600 °C, there will be different degrees of thermal cracking. Therefore, only manipulating the potential will not suffice to accomplish high selectivity. A protective gas environment and an appropriate catalyst surface interaction are also necessary.

Secondly, the activity and stability of a catalyst are also a challenge in that many organic molecules and their electrochemical intermediates can be corrosive or reactive, which can cause catalyst degradation and reduced activity over time. During the electrochemical conversion process, the electrode surfaces can become fouled or coated with reaction products, which can reduce the efficiency and selectivity of the process. Managing and mitigating electrode fouling can vary depending on the small organic molecules being converted. Another challenge in line is the development of the catalysts that are stable under the harsh electrochemical conditions and can maintain their activity over extended periods of time, since electrochemical reactions require

specialized catalysts to facilitate the conversion of small organic molecules into desired products.

Thirdly, fully unravelling reaction mechanisms remains as a difficult task as it has always been, due to the complex nature of electrochemical reactions involving organic molecules/intermediates, thermodynamics and kinetics. Nonetheless, a comprehensive understanding of the complex electrochemical processes at molecular and /or atomic level is essential to guide rational designs of the effective and efficient catalysts for electrochemical reactions, much research work is still needed in that regard.

Lastly, the mass transport limitations are also a roadblock. Efficient mass transport of small organic molecules to the catalyst surface is critical for achieving high conversion rates in electrochemical processes. However, small organic molecules can be bulky and have limited mobility in the electrolyte solution, which can result in mass transport limitations, leading to low conversion rates and reduced efficiency. Designing efficient mass transport pathways, optimizing electrode architectures, and managing diffusion limitations are the challenges that must be addressed to improve the performance of electrochemical systems for organic molecule conversion.

In addition, the scale-up of electrochemical processes for organic molecule conversion to commercial production levels can be challenging. The costs of materials, catalysts, and equipment, as well as the energy requirements for large-scale operations, need to be carefully considered and optimized for economic viability. Scale-up can also introduce engineering challenges related to reactor design, mass transfer, and process

control, which need to be addressed to enable cost-effective and scalable production of electricity and value-added chemicals from small organic molecules.

Response to the above challenges requires interdisciplinary research and development efforts involving expertise in electrochemistry, catalyst design, materials science/engineering, process optimization, and environmental sciences, among others. Overcoming these challenges will be crucial for advancing the field of electrochemical conversion of small organic molecules to electricity and value-added chemicals without CO₂ emission and realizing its potential for sustainable and environmentally friendly energy and chemical production.

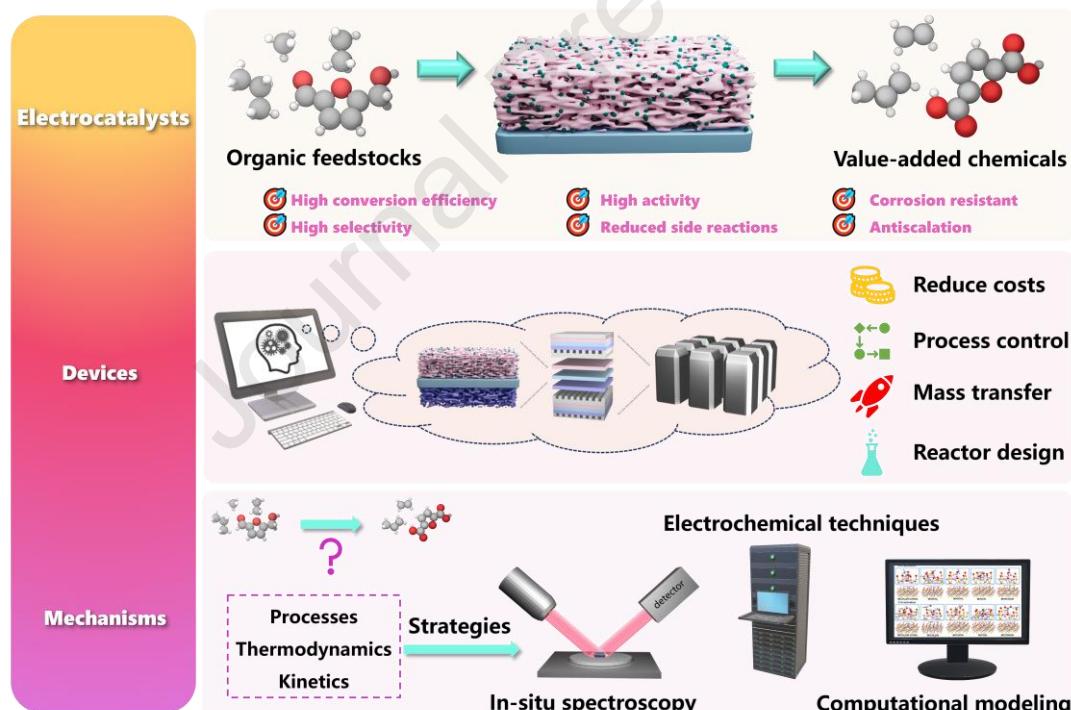


Fig. 9. The perspectives of the electrocatalysts, devices and mechanisms for the electrochemical conversion of small organic molecules.

Fig. 9 shows the perspectives of electrocatalysts, devices, and mechanisms for the electrochemical conversions of small organic molecules. One of the main areas of study for electrocatalysts is how to increase conversion efficiency and selectivity, increase

catalytic activity and specificity, and lessen the likelihood of side reactions. Reactor design is focused on cost reduction, precise process control, and enhanced mass transfer efficiency top priorities. Regarding mechanism research, a key area of interest is how to describe a substance's molecular mechanism at a molecular level using in-situ spectroscopy and contemporary artificial intelligence technologies.

7. Conclusions

In this review, the advances for electrochemical conversion of small organic molecules to hydrogen/electricity and value-added chemicals without CO₂ emission are summarized. The small organic molecules which are candidates for the electrochemical conversion are first introduced for wastewater treatment, alkane conversion, alcohol conversion, and biomass conversion. Then, the recent advances in the development of electrocatalysts are summarized. In terms of reaction potential and stability, noble metal catalysts clearly outperform non-precious metal catalysts. It is essential to develop novel catalysts with low reaction potential in order to lower the cost of the catalyst and increase its stability. Subsequently, a summary of reaction device design is provided. The special reaction system makes the device design more convenient since the main products of the reaction are respectively in liquid and gaseous states, eliminating the requirement for separation treatment. This is particularly advantageous for potential extensive industrial operations in the future. Furthermore, the reaction mechanisms are reviewed, the importance of this part lies in providing the fundamentals for rational design of electrocatalysts and reaction systems having high performance, high stability and high selectivity. Finally, the major challenges and potential future approaches are discussed. The insights into further development of the electrochemical conversion of small organic molecules to hydrogen/electricity and value-added chemicals without CO₂ emission are provided from the perspectives of both fundamental understanding and technological applications in the future.

Author contributions

J.-L. Luo and X.-Z. Fu proposed the concept. J.W. Liu wrote the manuscript. X.-Z. Fu and J.-L. Luo revised the manuscript. All authors participated in data analysis and manuscript discussion.

Competing financial interests

The authors declare no competing financial interests.

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References

- [1] X. Wu, Y. Wang, Z.-S. Wu, Design principle of electrocatalysts for the electrooxidation of organics, *Chem* 8 (2022) 2594–2629.
- [2] C. Xu, E. Paone, D. Rodríguez-Padrón, R. Luque, F. Mauriello, Recent catalytic routes for the preparation and the upgrading of biomass derived furfural and 5-hydroxymethylfurfural, *Chem. Soc. Rev.* 49 (2020) 4273–4306.
- [3] B. Huang, Z. Sun, G. Sun, Recent progress in cathodic reduction-enabled organic electrosynthesis: Trends, challenges, and opportunities, *eScience* 2 (2022) 243–277.
- [4] T. Wang, L. Tao, X. Zhu, C. Chen, W. Chen, S. Du, Y. Zhou, B. Zhou, D. Wang, C. Xie, P. Long, W. Li, Y. Wang, R. Chen, Y. Zou, X.-Z. Fu, Y. Li, X. Duan, S. Wang, Combined anodic and cathodic hydrogen production from aldehyde oxidation and hydrogen evolution reaction, *Nat. Catal.* 5 (2022) 66–73.

- [5] Z. Li, Y. Yan, S.-M. Xu, H. Zhou, M. Xu, L. Ma, M. Shao, X. Kong, B. Wang, L. Zheng, H. Duan, Alcohols electrooxidation coupled with H₂ production at high current densities promoted by a cooperative catalyst, *Nat. Commun.* 13 (2022) 147.
- [6] B. You, N. Jiang, X. Liu, Y. Sun, Simultaneous H₂ generation and biomass upgrading in water by an efficient noble-metal-free bifunctional electrocatalyst, *Angew. Chem. Int. Ed.* 55 (2016) 9913–9917.
- [7] A. R. Poerwoprajitno, L. Gloag, J. Watt, S. Cychy, S. Cheong, P. V. Kumar, T. M. Benedetti, C. Deng, K. Wu, C. E. Marjo, D. L. Huber, M. Muhler, J. J. Gooding, W. Schuhmann, D. Wang, R. D. Tilley, Faceted branched nickel nanoparticles with tunable branch length for high-activity electrocatalytic oxidation of biomass, *Angew. Chem. Int. Ed.* 59 (2020) 15487–15491.
- [8] Y. Yang, X. Wu, M. Ahmad, F. Si, S. Chen, C. Liu, Y. Zhang, L. Wang, J. Zhang, J. Luo, X. Fu, A direct formaldehyde fuel cell for CO₂-emission free co-generation of electrical energy and valuable chemical/hydrogen, *Angew. Chem. Int. Ed.* 62 (2023) e202302950.
- [9] C. Tang, R. Zhang, W. Lu, Z. Wang, D. Liu, S. Hao, G. Du, A. M. Asiri, X. Sun, Energy-saving electrolytic hydrogen generation: Ni₂P nanoarray as a high-performance non-noble-metal electrocatalyst, *Angew. Chem. Int. Ed.* 56 (2017) 842–846.
- [10] L. Wang, Y. Zhu, Y. Wen, S. Li, C. Cui, F. Ni, Y. Liu, H. Lin, Y. Li, H. Peng, B. Zhang, Regulating the local charge distribution of Ni active sites for the urea oxidation reaction, *Angew. Chem. Int. Ed.* 60 (2021) 10577–10582.
- [11] X. Hu, J. Zhu, J. Li, Q. Wu, Urea Electrooxidation: Current development and understanding of Ni-based catalysts, *ChemElectroChem* 7 (2020) 3211–3228.
- [12] W. Chen, L. Xu, X. Zhu, Y. Huang, W. Zhou, D. Wang, Y. Zhou, S. Du, Q. Li, C. Xie, L. Tao, C. Dong, J. Liu, Y. Wang, R. Chen, H. Su, C. Chen, Y. Zou, Y. Li, Q. Liu, S. Wang, Unveiling the electrooxidation of urea: intramolecular coupling of the N–N bond, *Angew. Chem. Int. Ed.* 60 (2021) 7297–7307.
- [13] S.-K. Geng, Y. Zheng, S.-Q. Li, H. Su, X. Zhao, J. Hu, H.-B. Shu, M. Jaroniec, P. Chen, Q.-H. Liu, S.-Z. Qiao, Nickel ferrocyanide as a high-performance urea oxidation electrocatalyst, *Nat. Energy* 6 (2021) 904–912.
- [14] V. Kyriakou, D. Neagu, G. Zafeiropoulos, R. K. Sharma, C. Tang, K. Kousi, I. S. Metcalfe, M. C. M. van de Sanden, M. N. Tsampas, Symmetrical exsolution of Rh nanoparticles in solid oxide cells for efficient syngas production from greenhouse gases, *ACS Catal.* 10 (2020) 1278–1288.
- [15] J. Li, J. Hou, X. Xi, Y. Lu, M. Li, Y. Fan, L. Wang, L. Wang, X.-Z. Fu, J.-L. Luo, Cogeneration of ethylene and electricity in symmetrical protonic solid oxide fuel cells based on a La_{0.6}Sr_{0.4}Fe_{0.8}Nb_{0.1}Cu_{0.1}O_{3-δ} electrode, *J. Mater. Chem. A* 8 (2020) 25978–25985.
- [16] S. Liu, K. T. Chuang, J.-L. Luo, Double-layered perovskite anode with *in situ* exsolution of a Co–Fe alloy to cogenerate ethylene and electricity in a proton-conducting ethane fuel cell, *ACS Catal.* 6 (2016) 760–768.
- [17] N. Shi, S. Xue, Y. Xie, Y. Yang, D. Huan, Y. Pan, R. Peng, C. Xia, Z. Zhan, Y. Lu, Co-generation of electricity and olefin via proton conducting fuel cells using (Pr_{0.3}Sr_{0.7})_{0.9}Ni_{0.1}Ti_{0.9}O₃ catalyst layers, *Appl. Catal. B Environ.* 272 (2020) 118973.
- [18] N. Yu, T. Liu, X. Chen, M. Miao, M. Ni, Y. Wang, Co-generation of liquid chemicals and electricity over Co–Fe alloy/perovskite anode catalyst in a propane fueled solid oxide fuel cell, *Sep. Purif. Technol.* 291 (2022) 120890.
- [19] X. Yan, Y. Yang, Y. Zeng, B. Shalchi Amirkhiz, J.-L. Luo, N. Yan, Generating C4 alkenes in solid

- oxide fuel cells via cofeeding H₂ and *n*-butane using a selective anode electrocatalyst, *ACS Appl. Mater. Interfaces* 12 (2020) 16209–16215.
- [20] K. Xiang, D. Wu, X. Deng, M. Li, S. Chen, P. Hao, X. Guo, J. Luo, X. Fu, Boosting H₂ generation coupled with selective oxidation of methanol into value-added chemicals over cobalt hydroxide@hydroxysulfide nanosheets electrocatalysts, *Adv. Funct. Mater.* 30 (2020) 1909610.
- [21] J. Zhang, Q. Zhang, X. Feng, Support and interface effects in water-splitting electrocatalysts, *Adv. Mater.* 31 (2019) 1808167.
- [22] J. Liu, Y. Guo, X.-Z. Fu, J.-L. Luo, C. Zhi, Strengthening absorption ability of Co–N–C as efficient bifunctional oxygen catalyst by modulating the d band center using MoC, *Green Energy Environ.* 8 (2023) 459–469.
- [23] X. Du, J. Huang, J. Zhang, Y. Yan, C. Wu, Y. Hu, C. Yan, T. Lei, W. Chen, C. Fan, J. Xiong, Modulating electronic structures of inorganic nanomaterials for efficient electrocatalytic water splitting, *Angew. Chem. Int. Ed.* 58 (2019) 4484–4502.
- [24] H. Ding, H. Liu, W. Chu, C. Wu, Y. Xie, Structural transformation of heterogeneous materials for electrocatalytic oxygen evolution reaction, *Chem. Rev.* 121 (2021) 13174–13212.
- [25] B. Zhao, J. Liu, C. Xu, R. Feng, P. Sui, J.-X. Luo, L. Wang, J. Zhang, J.-L. Luo, X.-Z. Fu, Interfacial engineering of Cu₂Se/Co₃Se₄ multivalent hetero-nanocrystals for energy-efficient electrocatalytic co-generation of value-added chemicals and hydrogen, *Appl. Catal. B Environ.* 285 (2021) 119800.
- [26] F. Si, S. Liu, Y. Liang, X.-Z. Fu, J. Zhang, J.-L. Luo, Fuel cell reactors for the clean cogeneration of electrical energy and value-added chemicals, *Electrochem. Energy Rev.* 5 (2022) 25.
- [27] S. Liu, Q. Liu, X.-Z. Fu, J.-L. Luo, Cogeneration of ethylene and energy in protonic fuel cell with an efficient and stable anode anchored with in-situ exsolved functional metal nanoparticles, *Appl. Catal. B Environ.* 220 (2018) 283–289.
- [28] J. Weidner, S. Barwe, K. Slizberg, S. Piontek, J. Masa, U.-P. Apfel, W. Schuhmann, Cobalt–metalloid alloys for electrochemical oxidation of 5-hydroxymethylfurfural as an alternative anode reaction in lieu of oxygen evolution during water splitting, *Beilstein J. Org. Chem.* 14 (2018) 1436–1445.
- [29] R. Li, K. Xiang, Z. Peng, Y. Zou, S. Wang, Recent advances on electrolysis for simultaneous generation of valuable chemicals at both anode and cathode, *Adv. Energy Mater.* 11 (2021) 2102292.
- [30] K. Ye, G. Wang, D. Cao, G. Wang, Recent advances in the electro-oxidation of urea for direct urea fuel cell and urea electrolysis, *Top. Curr. Chem.* 376 (2018) 42.
- [31] Z. Lai, L. Lee, H. Li, Electroreforming of biomass for value-added products, *Micromachines* 12 (2021) 1405.
- [32] R. K. Singh, K. Rajavelu, M. Montag, A. Schechter, advances in catalytic electrooxidation of urea: a review, *Energy Technol.* 9 (2021) 2100017.
- [33] Y. He, L. Deng, Y. Lee, K. Li, J. Lee, A Review on the critical role of H₂ donor in the selective hydrogenation of 5-hydroxymethylfurfural, *ChemSusChem* 15 (2022) e202200232.
- [34] Y.-R. Luo, *Comprehensive handbook of chemical bond energies*; CRC Press: Boca Raton, 2007.
- [35] F. Guo, K. Ye, M. Du, X. Huang, K. Cheng, G. Wang, D. Cao, Electrochemical impedance analysis of urea electro-oxidation mechanism on nickel catalyst in alkaline medium, *Electrochimica Acta* 210 (2016) 474–482.

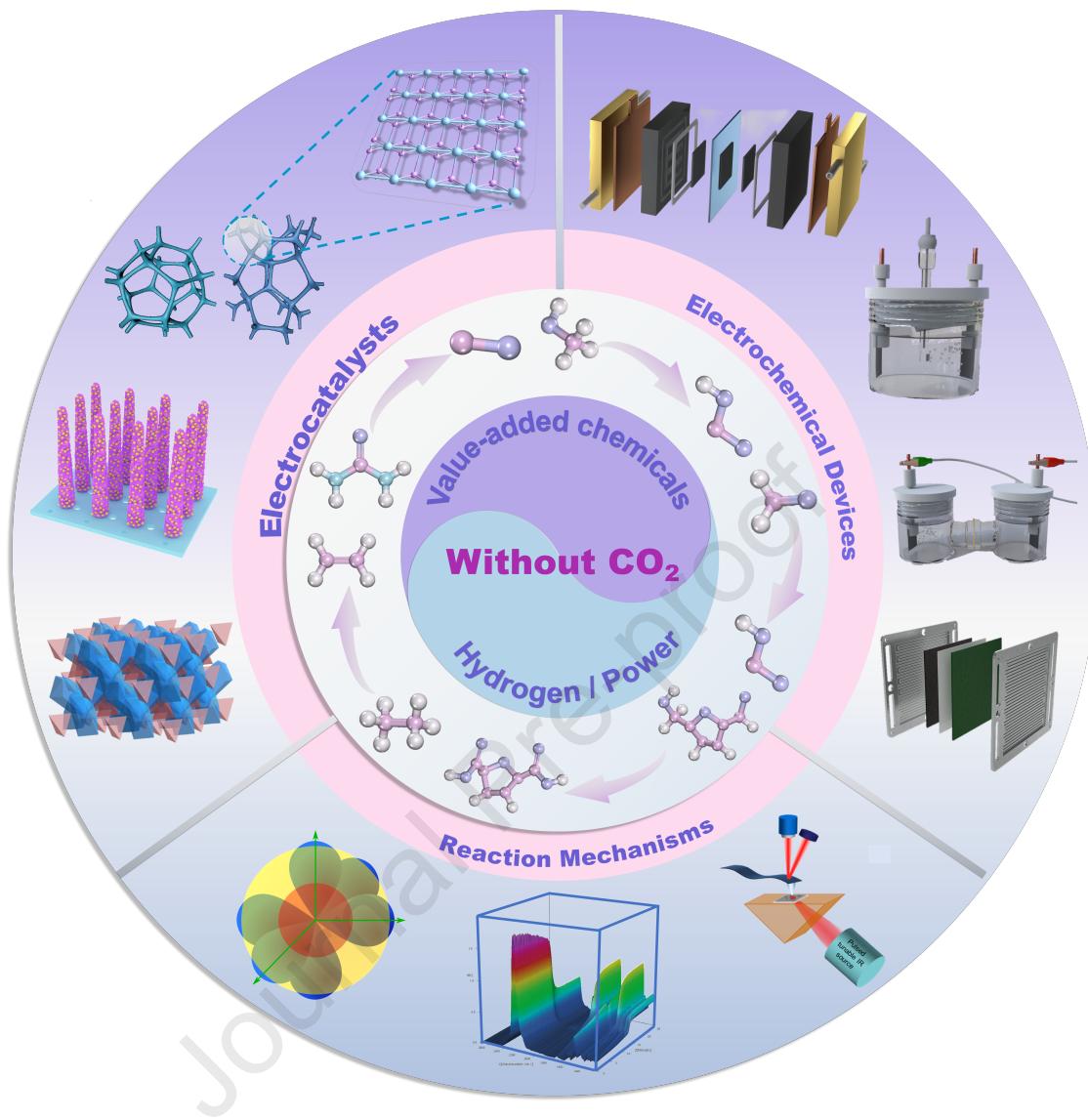
- [36] N. V. Rees, R. G. Compton, Carbon-free energy: a review of ammonia- and hydrazine-based electrochemical fuel cells, *Energy Environ. Sci.* 4 (2011) 1255–1260.
- [37] J. Wang, B. Zhang, W. Guo, L. Wang, J. Chen, H. Pan, W. Sun, Toward electrocatalytic methanol oxidation reaction: longstanding debates and emerging catalysts, *Adv. Mater.* 35 (2023) 2211099.
- [38] J. Xu, Z. Wang, Mechanistic investigations of electrochemical ethanol oxidation reaction by in situ raman spectroscopy, *ChemElectroChem* 10 (2023) e202300370.
- [39] G. Han, G. Li, Y. Sun, Electrocatalytic dual hydrogenation of organic substrates with a faradaic efficiency approaching 200%, *Nat. Catal.* 6 (2023) 224–233.
- [40] L. Gong, N. Agrawal, A. Roman, A. Holewinski, M. J. Janik, Density functional theory study of furfural electrochemical oxidation on the Pt (1 1 1) surface, *J. Catal.* 373 (2019) 322–335.
- [41] Y. Yang, T. Mu, Electrochemical oxidation of biomass derived 5-hydroxymethylfurfural (HMF): pathway, mechanism, catalysts and coupling reactions, *Green Chem.* 23 (2021) 4228–4254.
- [42] B. Zhao, J. Liu, X. Wang, C. Xu, P. Sui, R. Feng, L. Wang, J. Zhang, J.-L. Luo, X.-Z. Fu, CO₂-emission-free electrocatalytic CH₃OH selective upgrading with high productivity at large current densities for energy saved hydrogen co-generation, *Nano Energy* 80 (2021) 105530.
- [43] X. Deng, X. Kang, M. Li, K. Xiang, C. Wang, Z. Guo, J. Zhang, X.-Z. Fu, J.-L. Luo, Coupling efficient biomass upgrading with H₂ production via bifunctional Cu_xS@NiCo-LDH core–shell nanoarray electrocatalysts, *J. Mater. Chem. A* 8 (2020) 1138–1146.
- [44] Z.-Y. Yu, C.-C. Lang, M.-R. Gao, Y. Chen, Q.-Q. Fu, Y. Duan, S.-H. Yu, Ni–Mo–O nanorod-derived composite catalysts for efficient alkaline water-to-hydrogen conversion via urea electrolysis, *Energy Environ. Sci.* 11 (2018) 1890–1897.
- [45] X. Zhu, X. Dou, J. Dai, X. An, Y. Guo, L. Zhang, S. Tao, J. Zhao, W. Chu, X. C. Zeng, C. Wu, Y. Xie, Metallic nickel hydroxide nanosheets give superior electrocatalytic oxidation of urea for fuel cells, *Angew. Chem. Int. Ed.* 55 (2016) 12465–12469.
- [46] L. Zhang, L. Wang, H. Lin, Y. Liu, J. Ye, Y. Wen, A. Chen, L. Wang, F. Ni, Z. Zhou, S. Sun, Y. Li, B. Zhang, H. Peng, A lattice-oxygen-involved reaction pathway to boost urea oxidation, *Angew. Chem. Int. Ed.* 58 (2019) 16820–16825.
- [47] X. F. Lu, S. L. Zhang, W. L. Sim, S. Gao, X. W. (David) Lou, Phosphorized CoNi₂S₄ yolk-shell spheres for highly efficient hydrogen production via water and urea electrolysis, *Angew. Chem. Int. Ed.* 60 (2021) 22885–22891.
- [48] S. Chen, J. Duan, A. Vasileff, S. Z. Qiao, Size fractionation of two-dimensional sub-nanometer thin manganese dioxide crystals towards superior urea electrocatalytic conversion, *Angew. Chem. Int. Ed.* 55 (2016) 3804–3808.
- [49] J. Li, R. Wei, X. Wang, Y. Zuo, X. Han, J. Arbiol, J. Llorca, Y. Yang, A. Cabot, C. Cui, Selective methanol-to-formate electrocatalytic conversion on branched nickel carbide, *Angew. Chem. Int. Ed.* 59 (2020) 20826–20830.
- [50] G. Fu, X. Kang, Y. Zhang, X. Yang, L. Wang, X.-Z. Fu, J. Zhang, J.-L. Luo, J. Liu, Coordination effect-promoted durable ni(OH)₂ for energy-saving hydrogen evolution from water/methanol co-electrocatalysis, *Nano-Micro Lett.* 14 (2022) 200.
- [51] B. Zhao, J. Liu, C. Xu, R. Feng, P. Sui, L. Wang, J. Zhang, J. Luo, X. Fu, Hollow NiSe nanocrystals heterogenized with carbon nanotubes for efficient electrocatalytic methanol upgrading to boost hydrogen co-production, *Adv. Funct. Mater.* 31 (2021) 2008812.
- [52] Y. Zhou, Y. Shen, H. Li, Effects of metallic impurities in alkaline electrolytes on electro-

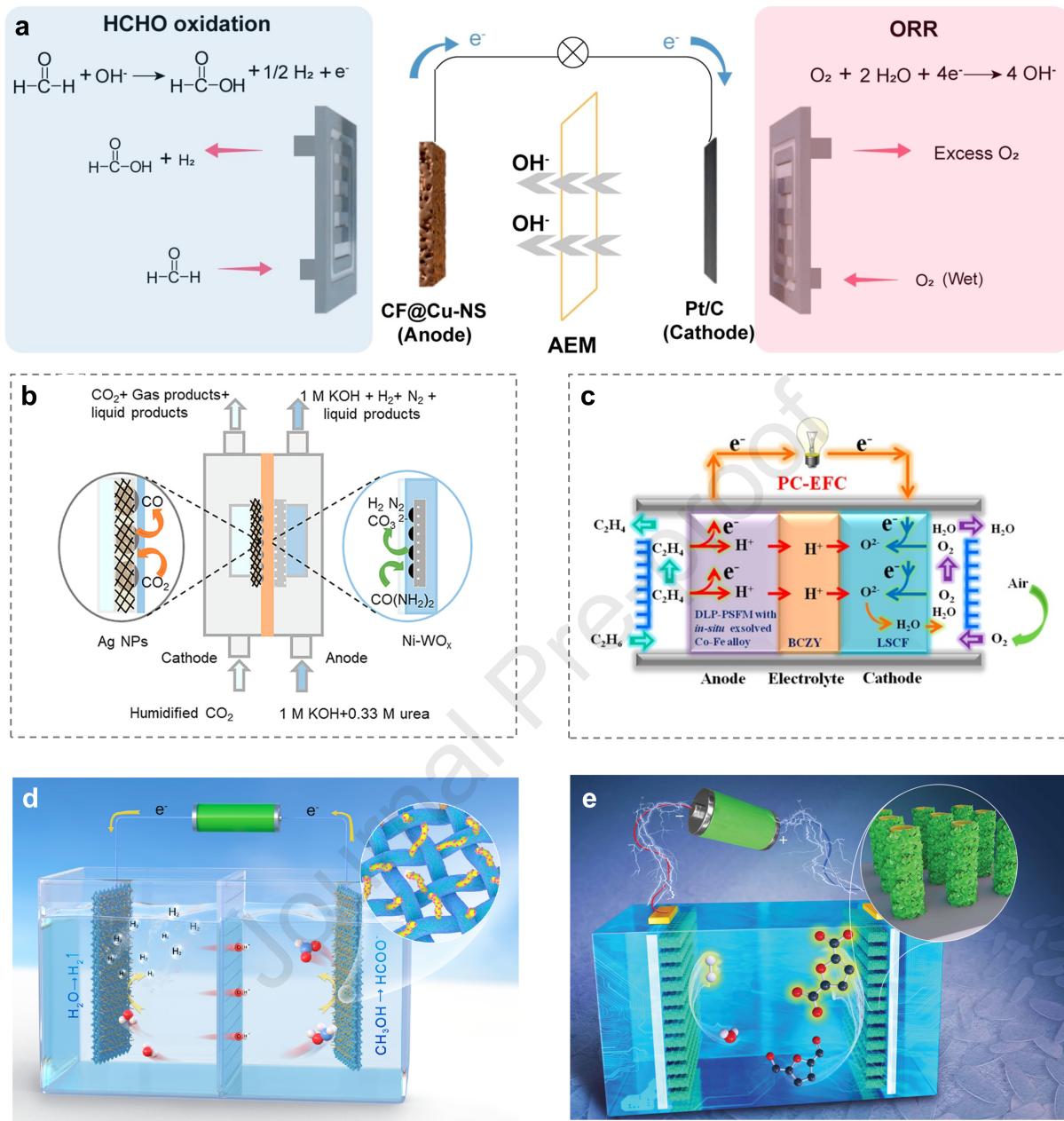
- oxidation of water and alcohol molecules, *J. Electrochem. Soc.* 168 (2021) 124516.
- [53] M. Yang, Z. Yuan, R. Peng, S. Wang, Y. Zou, Recent progress on electrocatalytic valorization of biomass-derived organics, *Energy Environ. Mater.* 5 (2022) 1117–1138.
- [54] J. Deng, H.-J. Song, M.-S. Cui, Y.-P. Du, Y. Fu, Aerobic oxidation of hydroxymethylfurfural and furfural by using heterogeneous $\text{Co}_x\text{O}_y\text{-N@C}$ catalysts, *ChemSusChem* 7 (2014) 3334–3340.
- [55] Y. Song, Z. Li, K. Fan, Z. Ren, W. Xie, Y. Yang, M. Shao, M. Wei, Ultrathin layered double hydroxides nanosheets array towards efficient electrooxidation of 5-hydroxymethylfurfural coupled with hydrogen generation, *Appl. Catal. B Environ.* 299 (2021) 120669.
- [56] G. Fu, X. Kang, Y. Zhang, Y. Guo, Z. Li, J. Liu, L. Wang, J. Zhang, X.-Z. Fu, J.-L. Luo, Capturing critical gem-diol intermediates and hydride transfer for anodic hydrogen production from 5-hydroxymethylfurfural, *Nat. Commun.* 14 (2023) 8395.
- [57] N. Heidary, N. Kornienko, *Operando* vibrational spectroscopy for electrochemical biomass valorization, *Chem. Commun.* 56 (2020) 8726–8734.
- [58] S. Li, R. Ma, J. Hu, Z. Li, L. Liu, X. Wang, Y. Lu, G. E. Sterbinsky, S. Liu, L. Zheng, J. Liu, D. Liu, J. Wang, Coordination environment tuning of nickel sites by oxyanions to optimize methanol electro-oxidation activity, *Nat. Commun.* 13 (2022) 2916.
- [59] Y. Qi, Y. Zhang, L. Yang, Y. Zhao, Y. Zhu, H. Jiang, C. Li, Insights into the activity of nickel boride/nickel heterostructures for efficient methanol electrooxidation, *Nat. Commun.* 13 (2022) 4602.
- [60] J. Liu, X. Yang, F. Si, B. Zhao, X. Xi, L. Wang, J. Zhang, X.-Z. Fu, J.-L. Luo, Interfacial component coupling effects towards precise heterostructure design for efficient electrocatalytic water splitting, *Nano Energy* 103 (2022) 107753.
- [61] Q. Xu, J. Zhang, H. Zhang, L. Zhang, L. Chen, Y. Hu, H. Jiang, C. Li, Atomic heterointerface engineering overcomes the activity limitation of electrocatalysts and promises highly-efficient alkaline water splitting, *Energy Environ. Sci.* 14 (2021) 5228–5259.
- [62] K. Xiang, Z. Song, D. Wu, X. Deng, X. Wang, W. You, Z. Peng, L. Wang, J.-L. Luo, X.-Z. Fu, Bifunctional Pt– Co_3O_4 electrocatalysts for simultaneous generation of hydrogen and formate *via* energy-saving alkaline seawater/methanol co-electrolysis, *J. Mater. Chem. A* 9 (2021) 6316–6324.
- [63] X. Wu, Y. Zhang, Y. Yang, G. Fu, F. Si, J. Chen, M. Ahmad, Z. Zhang, C. Ye, J. Zhang, X.-Z. Fu, J.-L. Luo, Ni_2P with phosphorus vacancy supported Pt clusters for efficiently electrocatalytic co-production of hydrogen and value-added chemicals from methanol-water at low potential, *Chem. Eng. J.* 452 (2023) 139057.
- [64] J. Hao, J. Liu, D. Wu, M. Chen, Y. Liang, Q. Wang, L. Wang, X.-Z. Fu, J.-L. Luo, In situ facile fabrication of $\text{Ni}(\text{OH})_2$ nanosheet arrays for electrocatalytic co-production of formate and hydrogen from methanol in alkaline solution, *Appl. Catal. B Environ.* 281 (2021) 119510.
- [65] Y. Yang, D. Xu, B. Zhang, Z. Xue, T. Mu, Substrate molecule adsorption energy: An activity descriptor for electrochemical oxidation of 5-Hydroxymethylfurfural (HMF), *Chem. Eng. J.* 433 (2022) 133842.
- [66] B. Zhao, J.-W. Liu, Y.-R. Yin, D. Wu, J.-L. Luo, X.-Z. Fu, Carbon nanofibers@NiSe core/sheath nanostructures as efficient electrocatalysts for integrating highly selective methanol conversion and less-energy intensive hydrogen production, *J. Mater. Chem. A* 7 (2019) 25878–25886.
- [67] L. Gao, Z. Liu, J. Ma, L. Zhong, Z. Song, J. Xu, S. Gan, D. Han, L. Niu, NiSe@NiOx core-shell

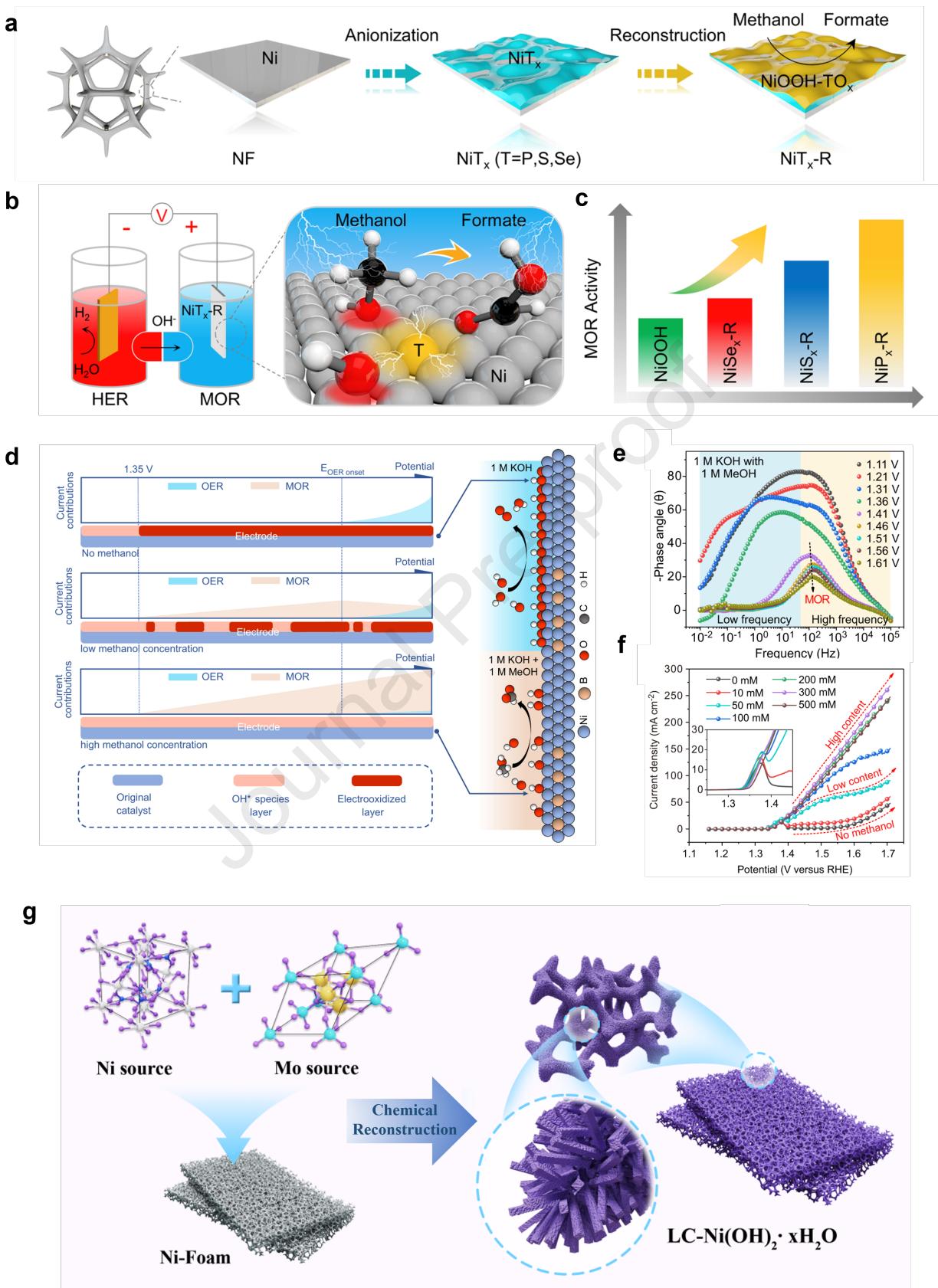
- nanowires as a non-precious electrocatalyst for upgrading 5-hydroxymethylfurfural into 2,5-furandicarboxylic acid, *Appl. Catal. B Environ.* 261 (2020) 118235.
- [68] M. Li, X. Deng, Y. Liang, K. Xiang, D. Wu, B. Zhao, H. Yang, J.-L. Luo, X.-Z. Fu, CoP@NiCo-LDH heteronanosheet arrays as efficient bifunctional electrocatalysts for co-generation of value-added formate and hydrogen with less-energy consumption, *J. Energy Chem.* 50 (2020) 314–323.
- [69] B. Zhao, C. Xu, M. Shakouri, R. Feng, Y. Zhang, J. Liu, L. Wang, J. Zhang, J.-L. Luo, X.-Z. Fu, Anode-cathode interchangeable strategy for *in situ* reviving electrocatalysts' critical active sites for highly stable methanol upgrading and hydrogen evolution reactions, *Appl. Catal. B Environ.* 305 (2022) 121082.
- [70] F. Si, J. Liu, Y. Zhang, B. Zhao, Y. Liang, X. Wu, X. Kang, X. Yang, J. Zhang, X. Fu, J. Luo, Surface spin enhanced high stable NiCo₂S₄ for energy-saving production of H₂ from water/methanol coelectrolysis at high current density, *Small* 19 (2023) 2205257.
- [71] B. Zhou, Y. Li, Y. Zou, W. Chen, W. Zhou, M. Song, Y. Wu, Y. Lu, J. Liu, Y. Wang, S. Wang, Platinum modulates redox properties and 5-hydroxymethylfurfural adsorption kinetics of Ni(OH)₂ for biomass upgrading, *Angew. Chem. Int. Ed.* 60 (2021) 22908–22914.
- [72] Y. Lu, C. Dong, Y. Huang, Y. Zou, Z. Liu, Y. Liu, Y. Li, N. He, J. Shi, S. Wang, Identifying the geometric site dependence of spinel oxides for the electrooxidation of 5-hydroxymethylfurfural, *Angew. Chem. Int. Ed.* 59 (2020) 19215–19221.
- [73] Y. Song, W. Xie, Y. Song, H. Li, S. Li, S. Jiang, J. Y. Lee, M. Shao, Bifunctional integrated electrode for high-efficient hydrogen production coupled with 5-hydroxymethylfurfural oxidation, *Appl. Catal. B Environ.* 312 (2022) 121400.
- [74] S. Barwe, J. Weidner, S. Cychy, D. M. Morales, S. Dieckhöfer, D. Hiltrop, J. Masa, M. Muhler, W. Schuhmann, Electrocatalytic oxidation of 5-(hydroxymethyl)furfural using high-surface-area nickel boride, *Angew. Chem. Int. Ed.* 57 (2018) 11460–11464.
- [75] R. Ge, Y. Wang, Z. Li, M. Xu, S. Xu, H. Zhou, K. Ji, F. Chen, J. Zhou, H. Duan, Selective electrooxidation of biomass-derived alcohols to aldehydes in a neutral medium: promoted water dissociation over a nickel-oxide-supported ruthenium single-atom catalyst, *Angew. Chem. Int. Ed.* 61 (2022) e202200211.
- [76] Z. Zhou, Y. Xie, L. Sun, Z. Wang, W. Wang, L. Jiang, X. Tao, L. Li, X.-H. Li, G. Zhao, Strain-induced *in situ* formation of NiOOH species on Co-Co bond for selective electrooxidation of 5-hydroxymethylfurfural and efficient hydrogen production, *Appl. Catal. B Environ.* 305 (2022) 121072.
- [77] B. Zhu, C. Chen, L. Huai, Z. Zhou, L. Wang, J. Zhang, 2,5-Bis(hydroxymethyl)furan: A new alternative to HMF for simultaneously electrocatalytic production of FDCA and H₂ over CoOOH/Ni electrodes, *Appl. Catal. B Environ.* 297 (2021) 120396.
- [78] X. Xi, J. Liu, Y. Fan, L. Wang, J. Li, M. Li, J.-L. Luo, X.-Z. Fu, Reducing d-p band coupling to enhance CO₂ electrocatalytic activity by Mg-doping in Sr₂FeMoO_{6-δ} double perovskite for high performance solid oxide electrolysis cells, *Nano Energy* 82 (2021) 105707.
- [79] X. Xi, J. Liu, W. Luo, Y. Fan, J. Zhang, J. Luo, X. Fu, Unraveling the enhanced kinetics of Sr₂Fe_{1+x}Mo_{1-x}O_{6-δ} electrocatalysts for high-performance solid oxide cells, *Adv. Energy Mater.* 11 (2021) 2102845.
- [80] D. Sarantarisidis, A. Atkinson, Redox cycling of Ni-based solid oxide fuel cell anodes: a review, *Fuel Cells* 7 (2007) 246–258.

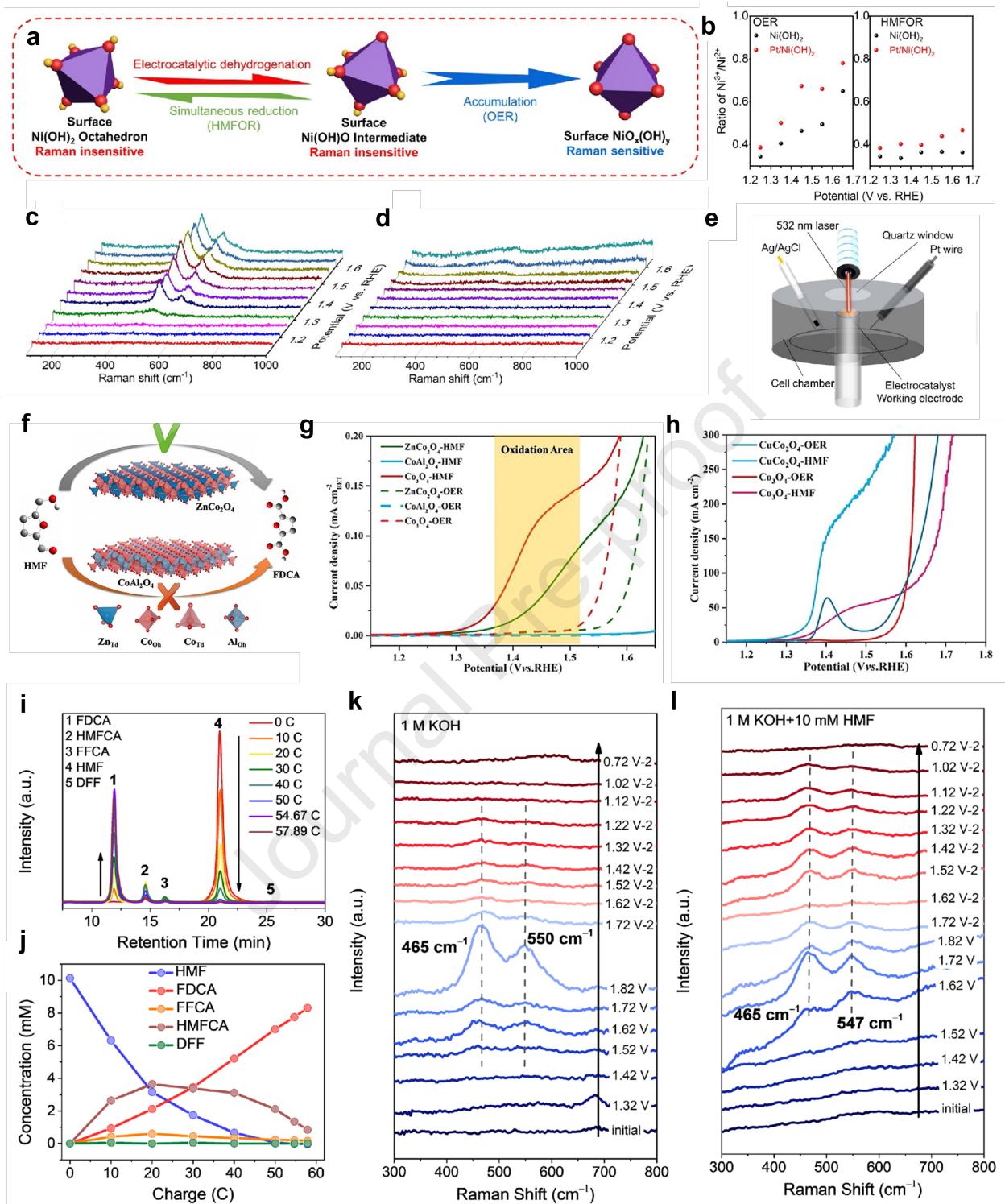
- [81] M. Pillai, Y. Lin, H. Zhu, R. J. Kee, S. A. Barnett, Stability and coking of direct-methane solid oxide fuel cells: effect of CO₂ and air additions, *J. Power Sources* 195 (2010) 271–279.
- [82] M. Qin, Y. Xiao, H. Yang, T. Tan, Z. Wang, X. Fan, C. Yang, Ru/Nb co-doped perovskite anode: achieving good coking resistance in hydrocarbon fuels via core-shell nanocatalysts exsolution, *Appl. Catal. B Environ.* 299 (2021) 120613.
- [83] T. Tan, Z. Wang, K. Huang, C. Yang, High-performance co-production of electricity and light olefins enabled by exsolved NiFe alloy nanoparticles from a double-perovskite oxide anode in solid oxide-ion-conducting fuel cells, *ACS Nano* 17 (2023) 13985–13996.
- [84] J. Yang, J. Zhou, Z. Liu, Y. Sun, C. Yin, K. Wang, R. Li, Z. Zhou, K. Wu, Exploring heterogeneous phases in highly A-site-deficient titanate with Ni exsolution, *J. Power Sources* 580 (2023) 233369.
- [85] H. Liu, T.-H. Lee, Y. Chen, E. W. Cochran, W. Li, Paired electrolysis of 5-(hydroxymethyl)furfural in flow cells with a high-performance oxide-derived silver cathode, *Green Chem.* 23 (2021) 5056–5063.
- [86] H. Liu, N. Agrawal, A. Ganguly, Y. Chen, J. Lee, J. Yu, W. Huang, M. Mbä Wright, M. J. Janik, W. Li, Ultra-low voltage bipolar hydrogen production from biomass-derived aldehydes and water in membrane-less electrolyzers, *Energy Environ. Sci.* 15 (2022) 4175–4189.
- [87] C. Wang, H.-J. Bongard, C. Weidenthaler, Y. Wu, F. Schüth, Design and application of a high-surface-area mesoporous δ-MnO₂ electrocatalyst for biomass oxidative valorization, *Chem. Mater.* 34 (2022) 3123–3132.
- [88] C. Chen, Z. Zhou, J. Liu, B. Zhu, H. Hu, Y. Yang, G. Chen, M. Gao, J. Zhang, Sustainable biomass upgrading coupled with H₂ generation over in-situ oxidized Co₃O₄ electrocatalysts, *Appl. Catal. B Environ.* 307 (2022) 121209.
- [89] P. Hauke, M. Klingenhof, X. Wang, J. F. de Araújo, P. Strasser, Efficient electrolysis of 5-hydroxymethylfurfural to the biopolymer-precursor furandicarboxylic acid in a zero-gap MEA-type electrolyzer, *Cell Rep. Phys. Sci.* 2 (2021) 100650.
- [90] X.-Z. Fu, J.-Y. Lin, S. Xu, J.-L. Luo, K. T. Chuang, A. R. Sanger, A. Krzywicki, CO₂ emission free co-generation of energy and ethylene in hydrocarbon SOFC reactors with a dehydrogenation anode, *Phys. Chem. Chem. Phys.* 13 (2011) 19615.
- [91] C. Cao, D. Ma, J. Jia, Q. Xu, X. Wu, Q. Zhu, Divergent Paths, Same Goal: A pair-electrosynthesis tactic for cost-efficient and exclusive formate production by metal–organic-framework-derived 2D electrocatalysts, *Adv. Mater.* 33 (2021) 2008631.
- [92] S. J. Smith, M. Lauria, L. Ahrens, P. McCleaf, P. Hollman, S. Bjälkefur Seroka, T. Hamers, H. P. H. Arp, K. Wiberg, Electrochemical oxidation for treatment of PFAS in contaminated water and fractionated foam—A pilot-scale study, *ACS EST Water* 3 (2023) 1201–1211.
- [93] J. Liu, W. Luo, Y. Yin, X.-Z. Fu, J.-L. Luo, Understanding the origin for propane non-oxidative dehydrogenation catalysed by d²-d⁸ transition metals, *J. Catal.* 396 (2021) 333–341.
- [94] H. Yuan, H. Liu, J. Du, K. Liu, T. Wang, L. Liu, Biocatalytic production of 2,5-furandicarboxylic acid: recent advances and future perspectives, *Appl. Microbiol. Biotechnol.* 104 (2020) 527–543.
- [95] J. Zhang, Y. Wang, C. Yang, S. Chen, Z. Li, Y. Cheng, H. Wang, Y. Xiang, S. Lu, S. Wang, Elucidating the electro-catalytic oxidation of hydrazine over carbon nanotube-based transition metal single atom catalysts, *Nano Res.* 14 (2021) 4650–4657.
- [96] H.-F. Wang, Z.-P. Liu, Comprehensive mechanism and structure-sensitivity of ethanol

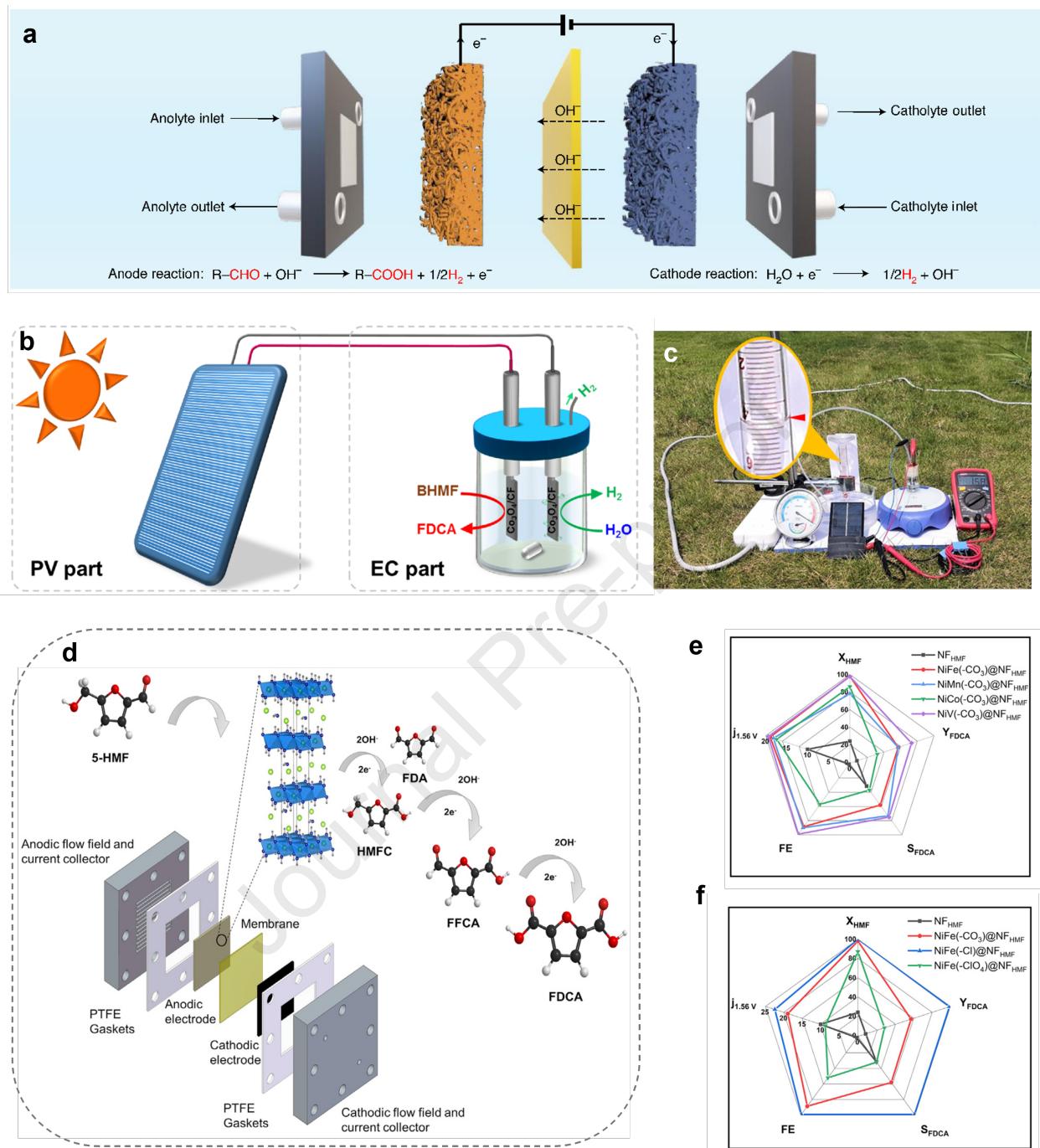
- oxidation on platinum: new transition-state searching method for resolving the complex reaction network, *J. Am. Chem. Soc.* 130 (2008) 10996–11004.
- [97] T. Wang, Z. Huang, T. Liu, L. Tao, J. Tian, K. Gu, X. Wei, P. Zhou, L. Gan, S. Du, Y. Zou, R. Chen, Y. Li, X.-Z. Fu, S. Wang, Transforming electrocatalytic biomass upgrading and hydrogen production from electricity input to electricity output, *Angew. Chem.* 134 (2022) e202115636.
- [98] Y. Yang, T. Mu, Electrochemical oxidation of biomass derived 5-hydroxymethylfurfural (HMF): pathway, mechanism, catalysts and coupling reactions, *Green Chem.* 23 (2021) 4228–4254.
- [99] X. Deng, G. Xu, Y. Zhang, L. Wang, J. Zhang, J. Li, X. Fu, J. Luo, Understanding the roles of electrogenerated Co^{3+} and Co^{4+} in selectivity-tuned 5-hydroxymethylfurfural oxidation, *Angew. Chem. Int. Ed.* 60 (2021) 20535–20542.

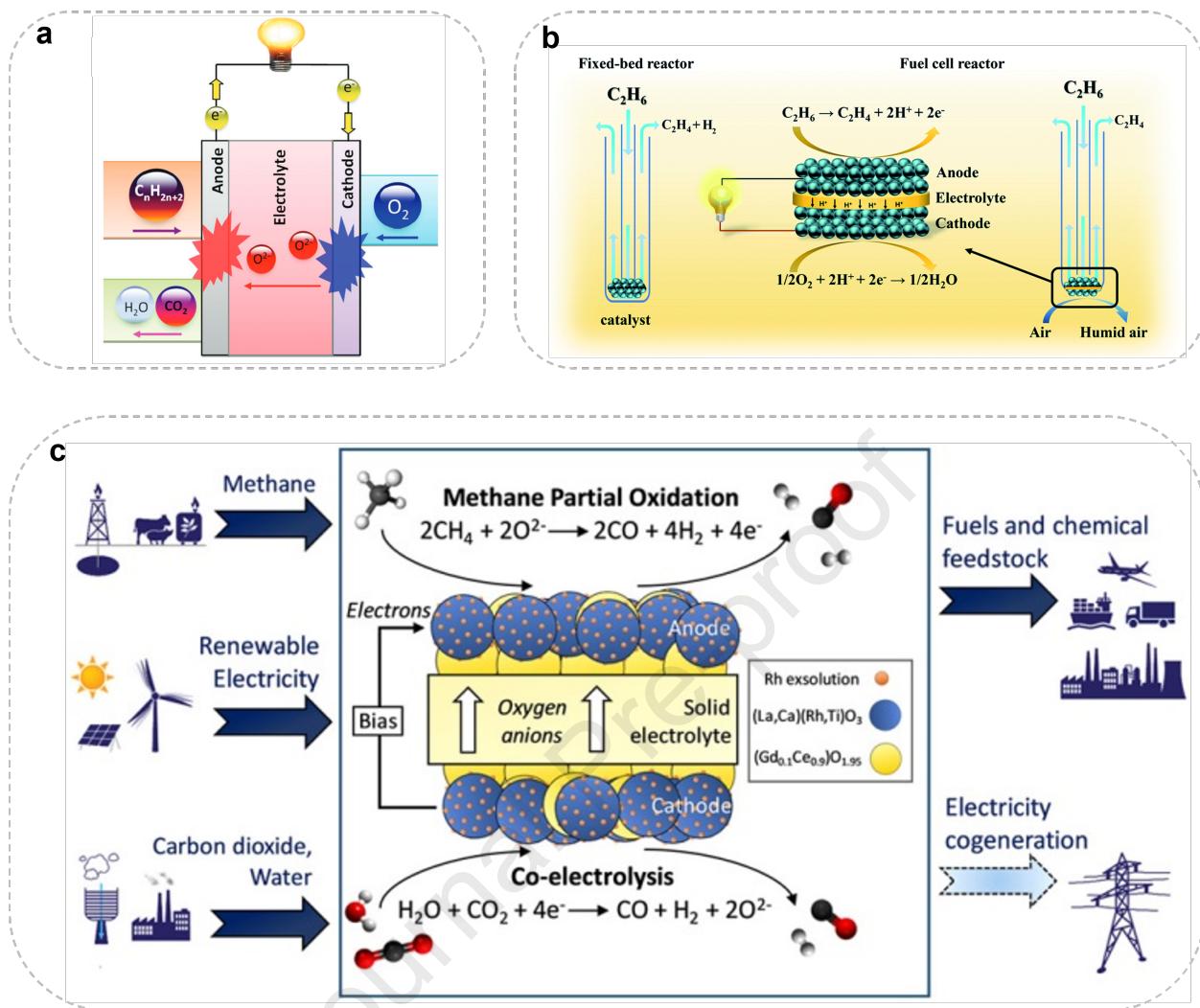


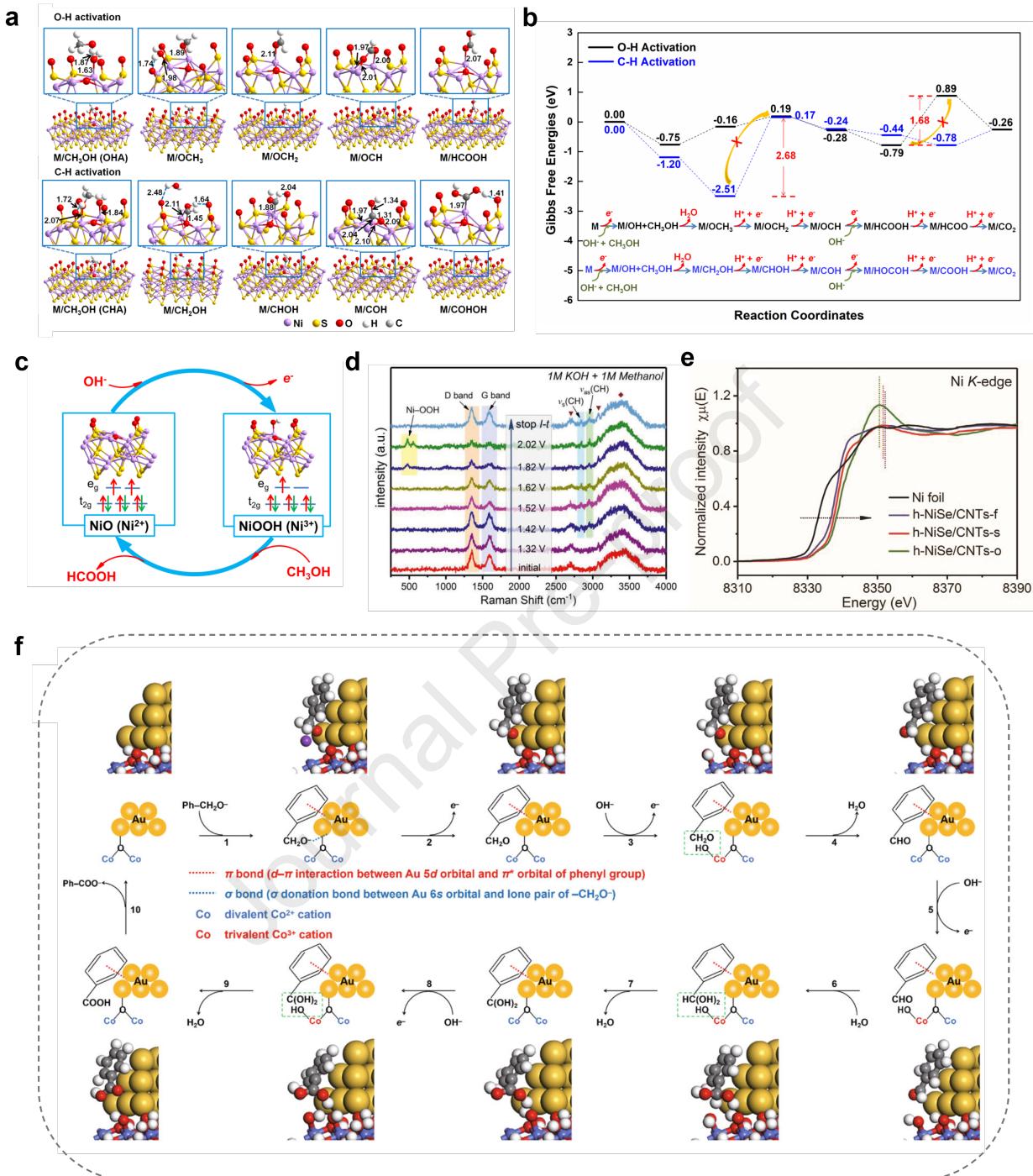


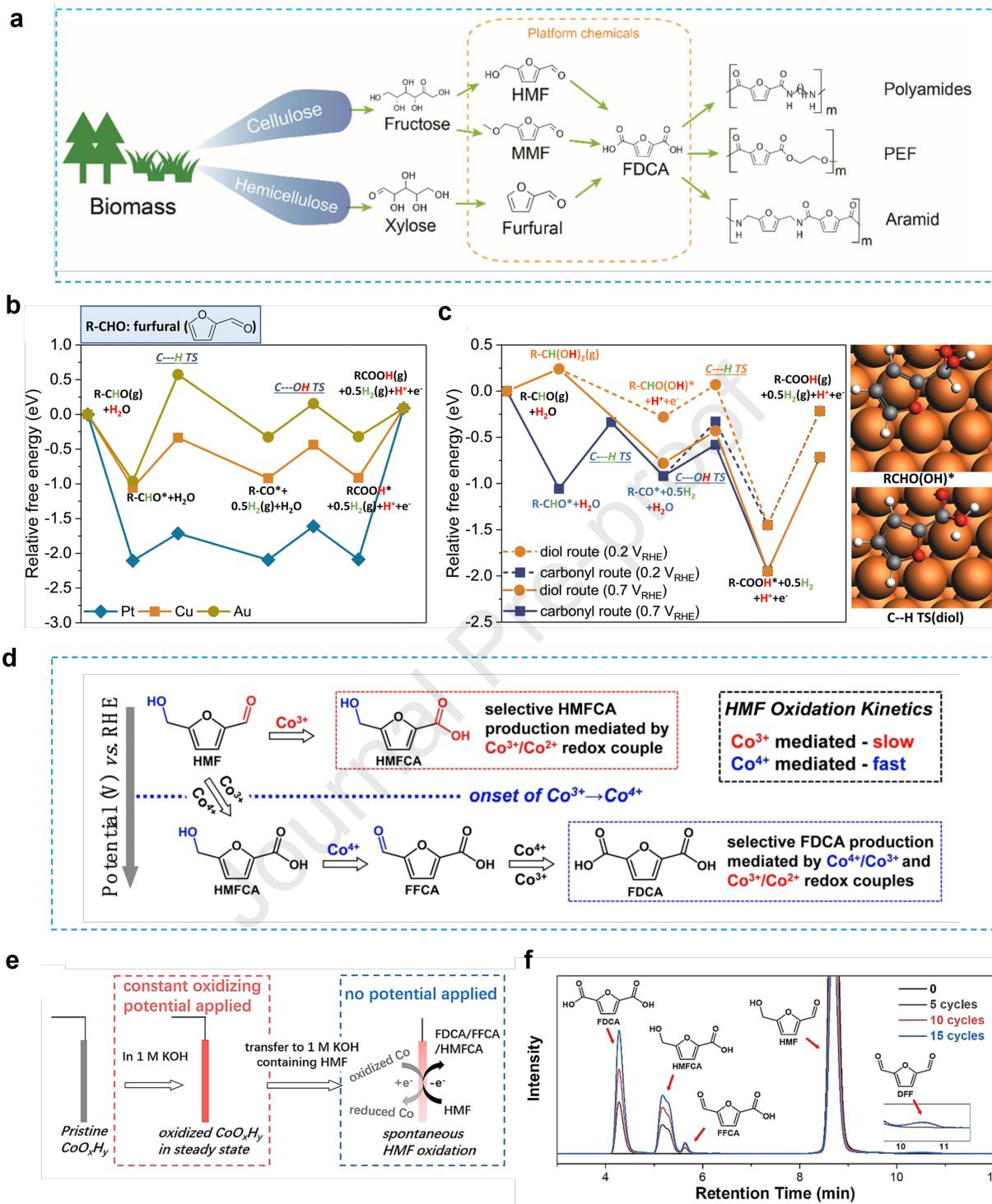


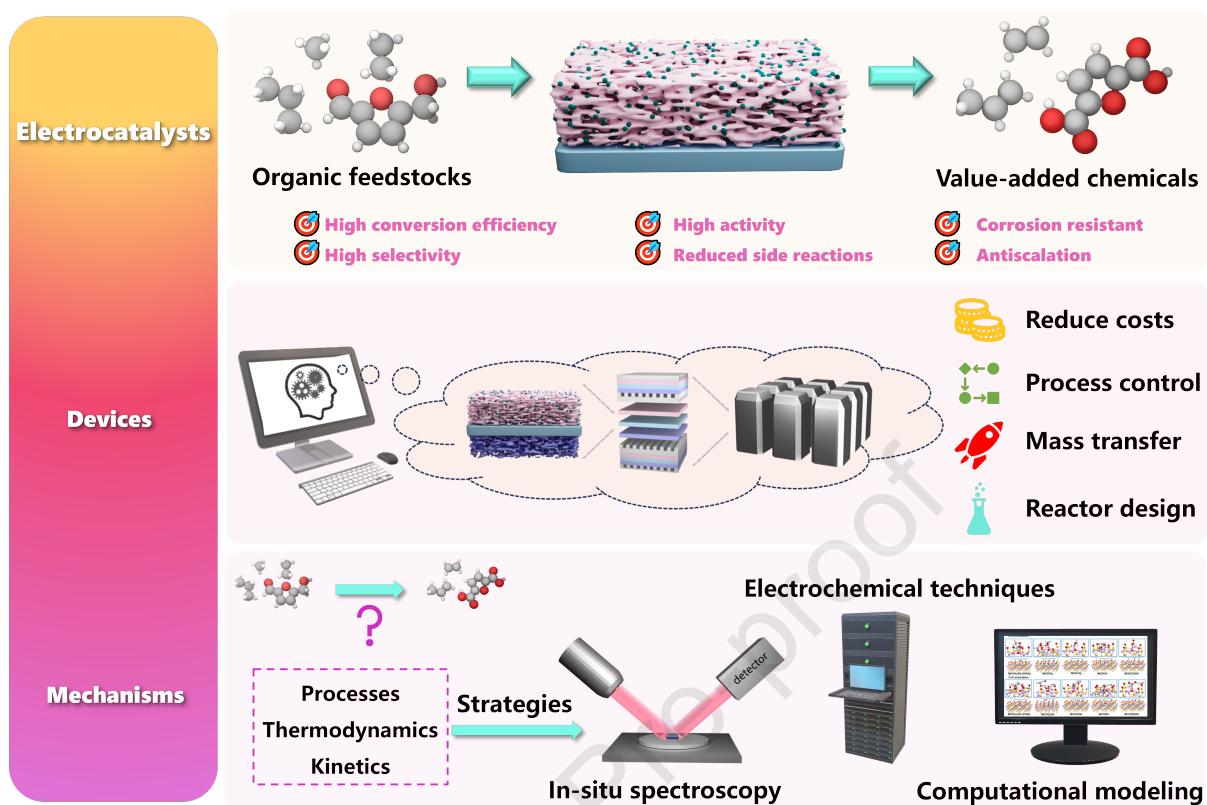












Highlights

- The recent advances in the electrochemical conversion of small organic molecules to value-added chemicals and hydrogen/electricity without CO₂ emission are summarized.
- It provides the fundamentals and insights for the rational design of electrocatalysts and reaction systems with high performance, high stability and high selectivity.

Declaration of interests

- 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.
- The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: