



Metal-phthalocyanine complexes as electrocatalysts for the multi-electron reduction of carbon dioxide

Zeliha Ertekin^{a,b}, Mark D. Symes^{a,*}

^a WestCHEM, School of Chemistry, University of Glasgow, Glasgow G12 8QQ, United Kingdom

^b Hacettepe University, Faculty of Science, Department of Chemistry, Beytepe, Ankara 06800, Turkey

ARTICLE INFO

Keywords:

Metal-phthalocyanine complex
CO₂ reduction
Electrocatalysis
Electroreduction

ABSTRACT

The electrocatalytic conversion of the greenhouse gas CO₂ to reduced products is an area of intensive research at the current time, as this offers a potential route for the production of synthetic fuels and chemical feedstocks from an abundant source. Among the various classes of catalysts explored for CO₂ electroreduction, metal-phthalocyanine compounds are amongst the most promising on account of their versatility and ease of functionalization. The majority of studies on these complexes report CO as the dominant product of CO₂ electroreduction. However, a number of recent studies have shown that certain metal-phthalocyanine complexes can catalyze multi-electron ($n > 2$) reductions of carbon dioxide, yielding products of higher value and utility than CO. However, there are remain opportunities for significant improvements in terms of Faradaic efficiencies and product selectivities. In this review, we provide a comprehensive overview of the latest advances in the development of metal-phthalocyanine catalysts for CO₂ reduction to products other than CO (with a particular emphasis on literature published since 2019). Our aim is to present a summary of the progress achieved thus far in this rapidly-evolving field and to offer insights and perspectives to guide future research efforts.

1. Introduction

The Paris Agreement, a legally binding international treaty on climate change adopted in 2015, recognizes the urgent need to limit global warming to well below 2 °C (relative to pre-industrial levels) and to pursue efforts to limit the temperature increase to 1.5 °C [1–5]. In response to this challenge, various technologies have been proposed to curtail rising CO₂ concentrations in the atmosphere, including electrochemical CO₂ reduction, which could allow the production and consumption of synthetic hydrocarbon fuels without increasing the overall amount of CO₂ in the atmosphere [6–9]. One of the most significant advantages of electrochemical CO₂ reduction is that it can operate at relatively low temperatures and pressure, making it a potentially more cost-effective and safer approach than other routes to synthetic hydrocarbons [10,11]. Furthermore, the electrochemical reduction process can be precisely controlled by adjusting the applied voltage, allowing (at least in theory) for the selective production of different chemicals/fuels [12,13]. Using renewable energy sources such as solar, geothermal, or wind energy to power the electrochemical cell would make electrochemical reduction a sustainable approach to CO₂ utilization [11,14,15].

A truly sustainable electrochemical CO₂ reduction process needs to be accompanied by a similarly sustainable anode process, so that the electrons and protons required for carbon dioxide reduction can be obtained in a fashion that does not lead to the production of pollutants or toxic waste. The oxidation of water is one such anode reaction, which has the further advantages that water is abundant on Earth and that the anode product is then O₂, which sets up a closed chemical cycle for when the hydrocarbon fuel is consumed. A schematic of such a cell for electrochemical carbon dioxide reduction in an aqueous solution is shown in Fig. 1a, where the electrode reactions can be summarized as in Eqs. 1 and 2:



Electrochemical CO₂ reduction can produce a wide range of products, depending on the reaction conditions. Fig. 1b shows some of the possible products that can be obtained along with the potentials at which these processes occur [16]. However, in many cases, there are significant kinetic barriers to forming these reduction products (particularly in the case of multi-electron processes) [17], which manifest in

* Corresponding author.

E-mail address: mark.symes@glasgow.ac.uk (M.D. Symes).

<https://doi.org/10.1016/j.apcata.2023.119388>

Received 8 June 2023; Received in revised form 15 August 2023; Accepted 21 August 2023

Available online 22 August 2023

0926-860X/© 2023 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/>).

the need for additional voltages over and above those displayed in Fig. 1b (so-called “overpotential”). Therefore, the development of electrocatalysts that can lower these overpotential barriers is essential if electrochemical CO₂ reduction is to become a viable prospect for large-scale fuel production.

In this regard, metal-phthalocyanine compounds (see Fig. 2) have been shown to exhibit high activity for the electroreduction of CO₂ to CO [16,18,19]. For example, Ma et al. demonstrated a nearly 100% Faradaic efficiency from -0.68 to -0.93 V_{RHE} for the conversion of CO₂ to CO by using pyrrolidinonyl Ni-phthalocyanine on carbon nanotubes [20]. In a similar study, Yang’s group utilized a bimetallic (Co-Fe) phthalocyanine heterostructure and achieved a 99% conversion efficiency of CO₂ to CO at -0.87 V_{RHE} [21]. Likewise, Wan and coworkers employed a Co-phthalocyanine-based gas diffusion electrode in a flow cell, resulting in a Faradaic efficiency for CO production of nearly 99% at -3.5 V vs Hg/HgO. On the basis of these results, it was postulated that various types of Co-phthalocyanine have the ability to achieve a Faradaic efficiency of over 90% for CO production across a wide range of electrode potential values from -0.9 to -0.4 V_{RHE} [22]. These findings demonstrate that phthalocyanine-based catalysts can enable efficient and selective CO₂ conversion to CO.

Recent review articles have discussed the process of reducing CO₂ to CO using phthalocyanine-based catalysts in some detail [16,18,23]. However, although CO could well prove a useful intermediate in a synthetic hydrocarbon production cycle, the direct reduction of CO₂ by more than two electrons (“deep reduction”) to products such as methanol, methane and C₂₊ hydrocarbons would arguably be even more attractive from an economic and sustainability perspective [24–26]. It is therefore noteworthy that metal-phthalocyanine complexes also display promising activity as heterogeneous molecular catalysts for the deep reduction of CO₂ [27]. However, despite a number of reports in recent years describing the use of metal-phthalocyanine electrocatalysts for the electrochemical conversion of CO₂ into reduction products other than CO, there has been no dedicated review of this field to date. Herein, we examine recent literature on this topic, with a particular emphasis on papers published since 2019. We focus on the main findings that have advanced this field, with an emphasis on the structural and functional diversity of these catalysts. Our goal is to inspire further research in this area by illustrating the broad potential of this class of electrocatalyst for CO₂ conversion.

2. Electrocatalytic CO₂ reduction with metal-phthalocyanine complexes

Metal-phthalocyanine complexes have been studied extensively for electrochemical CO₂ reduction as they are simple and cost-effective to synthesize, and chemically stable once formed [28]. The symmetrical electron distribution of the molecules makes them well-suited for

substrate adsorption, and the active site within their molecular structure facilitates effective surface modification [29,30]. The cathodic reduction potential of metal-phthalocyanine complexes can be shifted as a function of the metal ion and the substituents on the phthalocyanine ring. Other factors such as solvent, pH, and temperature can also influence the reduction potential, giving metal-phthalocyanine complexes a wide range of reduction potential values [31].

The general structure of metal-phthalocyanine complexes is illustrated in Fig. 2. These complexes give rise to characteristic electrochemical signals due to the electro-activity of their conjugated macrocyclic structures, whilst the N-donor atoms in the center of the structure provide an excellent binding site for numerous metal ions [32]. Phthalocyanine compounds can therefore be modified to enhance catalytic performance through tuning either (or both) the metal center and/or the phthalocyanine ring.

Metal-phthalocyanines are ideal materials for modifying electrodes to form heterogeneous catalyst systems for CO₂ reduction as their extended π -electron systems allow them to adsorb readily onto electrode surfaces. Such a strategy also circumvents the low solubility in aqueous solution that many metal-phthalocyanine complexes display, and which therefore renders them less effective as homogeneous catalysts [33]. Since most electrochemical CO₂ reduction processes involve multiple proton-coupled electron transfer steps [34], the transition metal is usually considered to be the active catalytic center in metal-phthalocyanine catalysts.

The initial CO₂ activation steps on metal phthalocyanines are as shown in Eqs. 3 and 4:



Where M^{II}-phthalocyanine represents the metal-phthalocyanine in its oxidized state and M^I-phthalocyanine represents the metal-phthalocyanine in its (one electron) reduced state. The first step generally involves the reduction of metal-phthalocyanine complexes that have been deposited on the electrode surface (Eq. 3). The second step as summarized by Eq. 4 is then held to be the rate-limiting step for the electrochemical reduction of CO₂ by metal-phthalocyanines, as judged by in situ scanning tunneling microscopy [35]. This study by Wang et al. determined that the CO₂ reduction process takes place primarily on the metal ions, but with the N centers coordinating to the metal also participating in the electrochemical reduction of CO₂.

According to literature studies, the proposed mechanism for the reduction of metal phthalocyanine complexes involves an initial one-electron reduction [36]. The reaction pathway and resulting product can be significantly influenced by both the active site of the catalyst and the surrounding reaction environment, with factors such as the choice of solvent or pH playing a critical role in determining the mechanism [37].

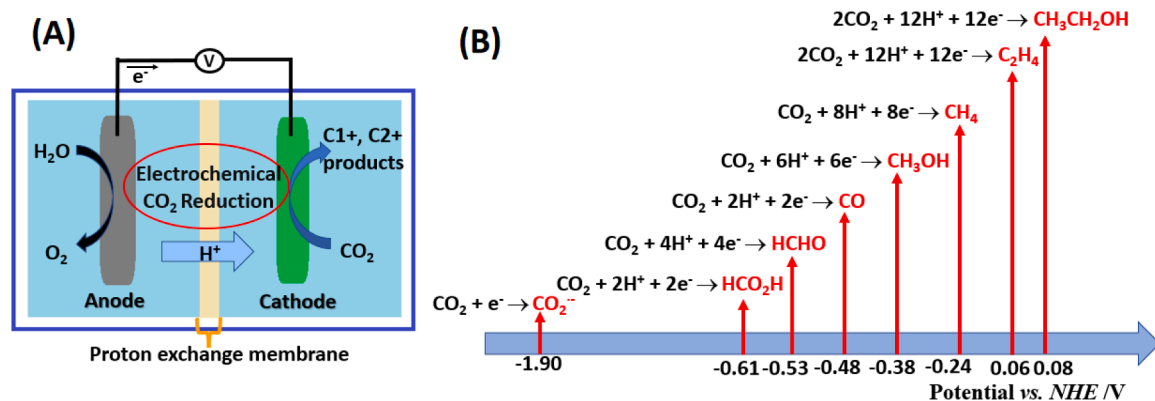


Fig. 1. a: Schematic representation of a cell for electrochemical CO₂ reduction in aqueous solution. 1b: A selection of possible CO₂ reduction processes and their equilibrium potentials vs. NHE (normal hydrogen electrode) at pH 7, 25 °C and 1 atm.

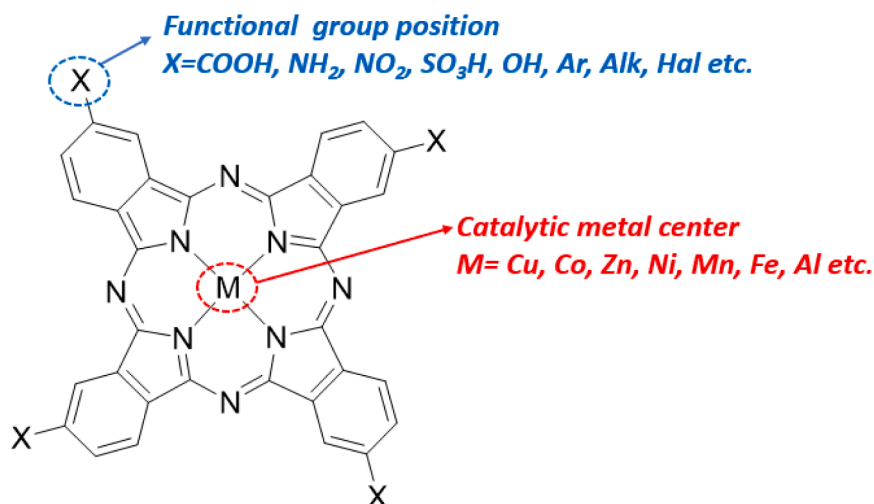


Fig. 2. An illustration of the generic phthalocyanine structure with a catalytic metal center (M) and positions for inserting functional groups onto the ring system (X) indicated.

Among the metal complexes, it is held that Co-phthalocyanine exhibits high activity for CO_2 reduction, while Zn-phthalocyanine shows the lowest activity [38,39]. Wu et al. [40] have reported a Zn(II) porphyrin complex for CO_2 electroreduction where in situ X-ray absorption spectroscopy suggested that the Zn ion remained in the 2+ oxidation state during the electrocatalytic CO_2 reduction process, with electrochemical studies further implying that the porphyrin ligand was the locus of the reduction reaction (i.e. the Zn center was redox-innocent).

The most commonly used metal-phthalocyanines for CO_2 reduction are based on Cu, Ni, Co, Fe, Mn and Zn, with the order of catalytic activity following the trend: $\text{Mn} > \text{Fe} > \text{Co} > \text{Zn} > \text{Cu} \sim \text{Ni}$ [32]. The catalytic activity of different metals in their respective phthalocyanine complexes is closely related to their redox potential, and it has been suggested that metal-phthalocyanine complexes with modestly cathodic potential values are the most active for CO_2 reduction [32]. However, predicting the optimal redox potential value for metal-phthalocyanines for CO_2 reduction is challenging because the applied potential has a significant impact on the distribution of the CO_2 reduction products. For instance, a reduction with a more negative potential (between -0.6 and -1.0 V vs. RHE) can favor the production of C_2H_4 , whereas a more positive potential value of $+0.016$ V vs. RHE may promote the formation of CO [41].

In terms of the deep reduction of carbon dioxide, Boutin et al. were the first to demonstrate that Co-phthalocyanine (on multi-wall carbon nanotubes) can catalyze the conversion of CO_2 to methanol in an

aqueous medium under ambient temperature and pressure conditions [29]. In the electrochemical conversion of CO_2 to CH_3OH , CO_2 is firstly reduced by two electrons to form CO, which is then further reduced by another four electrons to form CH_3OH (see Fig. 3). Additionally, it was determined that formaldehyde (HCHO) played a role as an intermediate on the pathway to CH_3OH in certain circumstances [42]. When the pH value and electrode potential were adjusted to maximize each partial reduction process, the Faradaic efficiency of CO_2 electrocatalytic reduction to CH_3OH was calculated as up to 20%, depending on the pathway [29]. Since this pioneering work, many studies have been conducted to further investigate this reaction. However, most of these studies have obtained a high yield of CO, with a relatively low yield of other carbon products [29,43].

In the literature, it is commonly reported that most metal-phthalocyanine complexes afford CO selectively as the two-electron reduction product. Several of the various possible reaction mechanisms that have been proposed for this process are summarized in Fig. 4 [44–46]. There are two general sets of pathways for the conversion of CO_2 to CO. The first involves the interaction of CO_2 with the metal center (pathway 1,2 in Fig. 4), while the second involves the protonation of the nitrogen group in the phthalocyanine (pathway 3,4,5 in Fig. 4). In both pathways, COOH^* is obtained as a key intermediate [37]. The dependence of these pathways on the pH value is critical for understanding the mechanism, as illustrated in Fig. 4. These proposed mechanisms have been obtained largely using Density Functional Theory (DFT) methods.

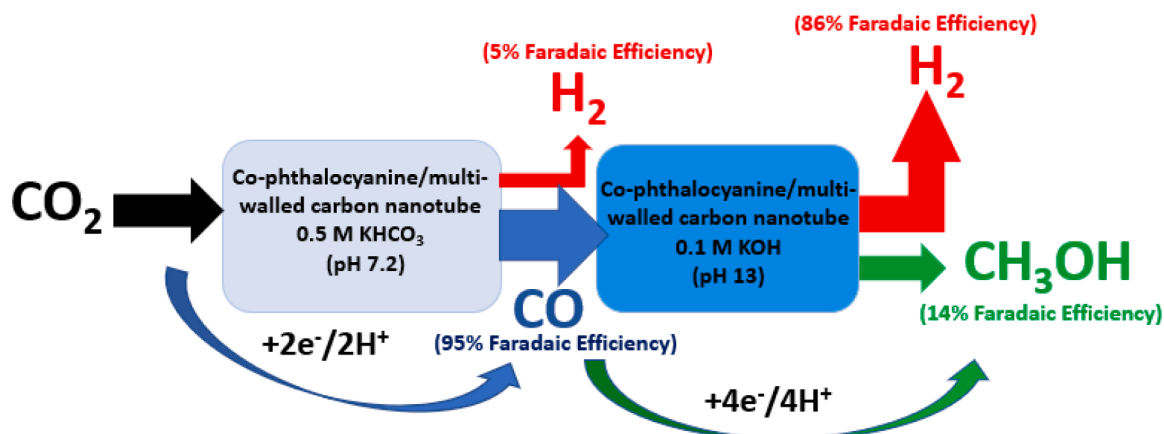


Fig. 3. Sequential electrochemical reduction of CO_2 to CH_3OH using cobalt phthalocyanine complexes on multi-walled carbon nanotube electrodes [29].

Table 1
Summary of metal-phthalocyanine complexes reported as electrocatalysts for CO₂ reduction to products other than CO during the period 2019–2023.

Entry	Electrocatalyst	Method of CO ₂ reduction	Cathode substrate	Electrolyte	pH	Potential / V vs NHE	Main product (s)	Faradaic Efficiency (%)	Current density / mA cm ⁻²	TOF / s ⁻¹	Electrochemical cell design	Ref.
1	NH ₂ -substituted Co-phthalocyanine/carbon nanotube	Electrochemical	Carbon fiber paper	0.1 M KHCO ₃	6.8	−1.00	CH ₃ OH	32	10	-	Two-compartment cell	Wu et al. [49]
2	Zn-phthalocyanine /carbon nitride	Photoelectrochemical	Fluorine doped tin oxide	0.1 M KHCO ₃	6.8	−1.00	CH ₃ OH HCOOH	- -	-	0.17	Double-cell reactor with circulating water	Zheng et al. [51]
3	Co-phthalocyanine /multi-walled carbon nanotube	Electrochemical	Carbon paper	0.1 M KOH	13.0	−0.14	CH ₃ OH	28	0.6	-	Photovoltaic-driven cell	Wang et al. [52]
4	Cu-phthalocyanine /carbon black	Electrochemical	Carbon paper	0.5 M KCl	-	−1.50	CH ₄ C ₂ H ₄ HCOOH CH ₃ CH ₂ OH CH ₄	6.0 6.0 10.0 15.0 52 ± 4	5.9	-	H-cell	Latiff et al. [43]
5	Cu- phthalocyanine	Electrochemical	Glassy carbon electrode	0.1 M KHCO ₃	6.8	-	CH ₄	15	19.9 ± 2.1	-	H-cell	Zhao et al. [53]
6	Co-phthalocyanine /Zinc-Nitrogen-Carbon tandem	Electrochemical	Gas diffusion electrode	1.0 M KOH	14.0	−1.15	CH ₄	15	19.9 ± 2.1	-	Flow cell	Lin et al. [54]
7	Phthalocyanine-Cu-(OH) ₂ / CuO ₄ nodes	Electrochemical	Glassy carbon electrode	0.1 M KHCO ₃	-	−1.20	C ₂ H ₄	50	7.3	-	H-cell	Qiu et al. [41]
8	Heat-treated Cu-phthalocyanine/carbon	Electrochemical	Copper foil	0.5 M KHCO ₃	-	−0.40	C ₂ H ₄	43	8.0	-	H-cell	Li et al. [55]
9	Sn-phthalocyanine dichloride/carbon nanotubes	Electrochemical	Carbon paper	0.5 M NaHCO ₃	-	−0.90	HCOOH	83	-	8.8	H-cell	Acharjya et al. [56]
10	Co- phthalocyanine	Electrochemical	Carbon paper	0.5 M KHCO ₃	7.2	−0.88	CH ₃ OH	0.3	0.03	-	Three-electrode cell	Boutin et al. [29]
11	Au-modulated Cu- phthalocyanine	Photoelectrochemical	BiVO ₄ nanosheet	0.1 M Na ₂ SO ₄	-	-	CH ₄	-	-	-	Three-electrode cell	Bian et al. [57]
12	Zn-phthalocyanine /perylene diimide	Photoelectrochemical	Prepared film	0.5 M Na ₂ SO ₄	7.0	−0.33	CH ₄	-	-	-	Cylindrical steel reactor	Sun et al. [58]
13	Cu-phthalocyanine /graphene/g-C ₃ N ₄	Photoelectrochemical	Fluorine doped tin oxide	0.2 M Na ₂ SO ₄	-	-	CH ₄	-	-	0.91	Three-electrode cell	Kang et al. [59]
14	Phthalocyanine-Cu-tetrafluoroterephthalonitrile	Electrochemical	Gas diffusion electrode	0.1 M KHCO ₃	-	−0.80	(HCOOH + CH ₃ COOH)	90	12.5	-	Flow-cell	Qiu et al. [60]
15	Co-phthalocyanine tetrasulfonamide/ carboxylated graphene oxide	Photoelectrochemical	Fluorine doped tin oxide	0.1 M KHCO ₃	-	−0.80	HCOO ⁻	84	1.5	-	One-compartment cell	Nandal et al. [61]
16	Fe-phthalocyanine /silicon carbide derived carbon	Bio-electroreduction	Activated carbon fiber	0.1 M NaHCO ₃	-	−0.70	HCOO ⁻	58	0.5	-	Double-chambered microbial electrolysis system	Singh et al. [62]

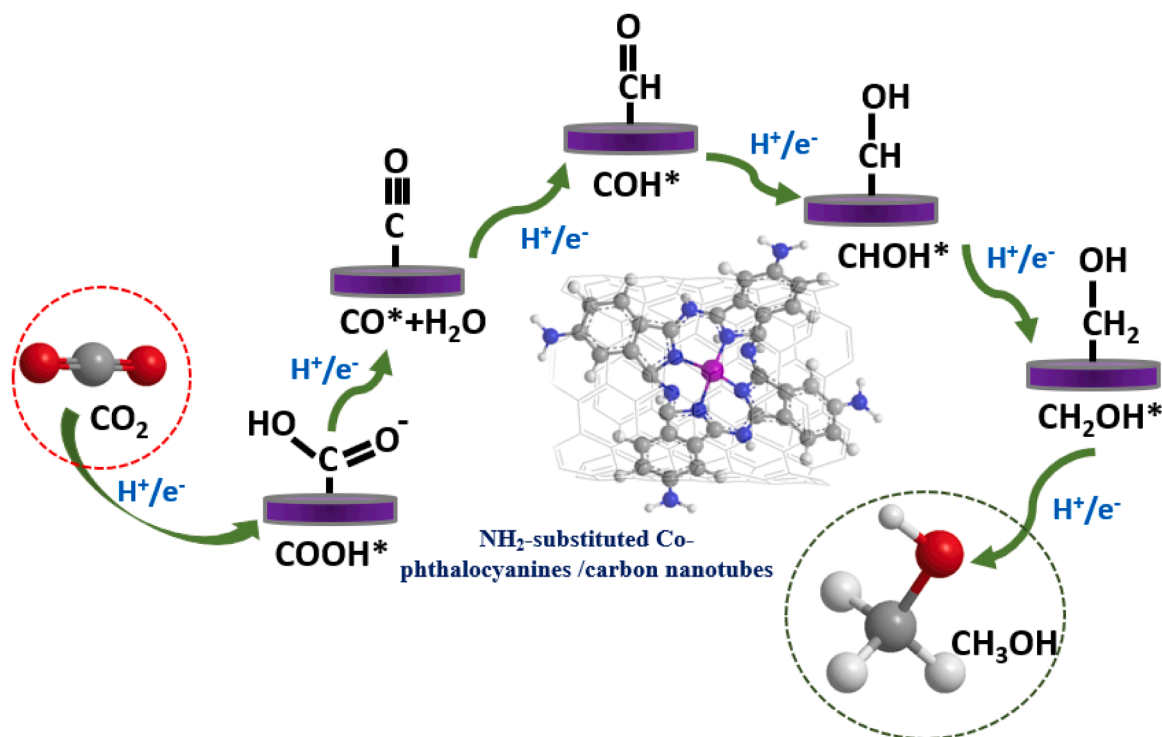


Fig. 5. Proposed reaction pathway for the electrochemical reduction of CO₂ to CH₃OH using NH₂-substituted Co-phthalocyanines supported on carbon nanotubes.

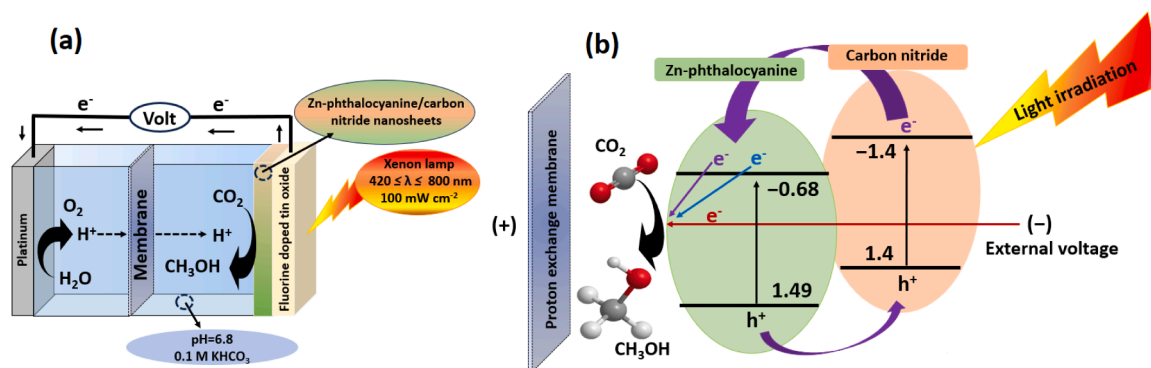


Fig. 6. a: A schematic representation of the photoelectrochemical CO₂ reduction cell. 6b: The proposed electron transfer route between carbon nitride nanosheets and Zn-phthalocyanine under irradiation.

Adapted from reference [51].

provide some of the energy required for CO₂ reduction and found that the reduction of CO₂ to methanol in an aqueous solution using a carbon electrode loaded with Co-phthalocyanine complexes showed an overall 28% Faradaic efficiency taking into account a two-step procedure, with the first step being CO₂ reduction to CO (with Faradaic efficiency of 95%), followed by reduction of CO to CH₃OH with a Faradaic efficiency of 21% (Table 1, Entry 3) [52].

In metal-phthalocyanine complexes, the selection of the support material for the catalysts is crucial, as it serves as both an anchor point and an electron source, strongly influencing the catalyst's function. Carbon supports are commonly used, with activated carbon, graphene oxide, carbon nanotubes and carbon black all having been employed. For example, Latiff et al. proposed that Cu-phthalocyanines supported on carbon nanotubes and carbon black give a higher Faradaic efficiency for C1 and C2 products (CO, HCOOH, CH₄, C₂H₄ and CH₃CH₂OH) than Cu-phthalocyanines supported on graphene oxide or activated carbon, and proposed an order of activity for Cu-phthalocyanines on carbon supports as follows: carbon black > carbon nanotubes > activated

carbon > graphene oxide (Table 1, Entry 4), which was found to match the order of electrical conductivity (with carbon black and carbon nanotubes being the more conductive substrates) [43]. The dimensions of the carbon support were also held to be a key determinant for the CO₂ electroreduction activity of the supported Cu-phthalocyanine complexes. Nanotubes that were long and thin (in the range of 10–30 nm in diameter and 10–30 μm in length) were found to be more effective compared to shorter and thicker structures, which was attributed to the fact that long and thin nanotubes were found to have the lowest charge transfer resistance (R_{ct}) by electrochemical impedance spectroscopy and to exhibit a larger electrochemical surface area compared to shorter and thicker nanotubes [63]. Furthermore, it was found that Cu-phthalocyanine complexes supported on thick and short carbon nanotubes produced H₂ as the main reduction product (Faradaic efficiency = 99%), while Cu-phthalocyanine complexes supported on long and thin carbon nanotubes produced more products of CO₂ reduction such as CO, HCOOH, CH₄, C₂H₄ and CH₃CH₂OH. Carbon black-Cu-phthalocyanine had a higher carbon product conversion

(81.8%) as compared to Cu-phthalocyanines supported on carbon nanotubes (66.3%) [43]. FTIR and XPS data were collected on the as-prepared materials, suggesting that the Cu-phthalocyanine complexes remained intact on the surface of the nanotubes. However, no analysis of the materials was conducted after the catalytic process. This potentially throws some doubt over the conclusions of this work, as several authors have reported that metallic Cu clusters, derived from Cu-phthalocyanines, are the active species in other CO₂ electro-reduction processes [64–66]. Furthermore, Lyu et al. [67] have shown that traces of Cu as low as 0.042 μg cm⁻² can act as an effective CO₂ electro-reduction catalyst, leading to potentially spurious results if the effects of trace metal impurities (or decomposition of molecular catalysts) are not properly considered.

It is known that the activity and selectivity of electrochemical CO₂ reduction is influenced by a range of factors, including the structure and composition of the catalyst, the electrolyte, the pH, and the design of the electrochemical cell [11]. It is possible to obtain electrochemical CO₂ products beyond two electron-reduced species such as CO and HCOOH using unmodified phthalocyanine compounds. For example, CO₂ reduction was tested in a H-cell using commercial Cu-phthalocyanine as an electrocatalyst, giving a maximum Faradaic efficiency for CH₄ production of 52 ± 4% and a turnover frequency of 659 h⁻¹ at -1.23 V_{RHE} (Table 1, Entry 5) [53].

Metal-nitrogen active sites embedded in carbon have shown remarkable Faradaic efficiencies for electrochemical CO₂ reduction [68]. These materials can enhance the activity of metal-phthalocyanine compounds beyond that which can be achieved with traditional carbon supports, offering additional sites for CO₂ activation, improved catalyst stability, and increased selectivity towards desired products. For example, Lin et al. synthesized a tandem catalyst (metal-nitrogen-active sites embedded in carbon) containing Co-phthalocyanine and zinc-nitrogen-carbon and found that this catalyst combination showed a greater than 100 times improvement in the relative CH₄/CO production rate compared to either Co-phthalocyanine or zinc-nitrogen-carbon on their own (Table 1, Entry 6) [54]. It was suggested that this type of tandem catalyst overcomes the constraint of linear scaling relationships for the adsorption of key intermediates, leading to a remarkable increase in the selectivity for primary C₁ and C₂₊ products that are reduced by more than two electrons. The obtained experimental results were corroborated by DFT analysis, highlighting a synergistic effect between the Co-phthalocyanine and the Zn-N-C structure. This revealed a sequential process, wherein the Zn-N-C surface actively contributed to the reduction of *CO to CH₄. It was shown that the reaction kinetics of

*CO hydrogenation were more favorable with a tandem catalyst than with Co-phthalocyanine alone and that the CO hydrogenation rate was approximately twice as high as that of CO₂ hydrogenation on the tandem catalyst [69]. The suggested reaction pathways are summarized in Fig. 7. It was proposed that the initial step in the process involved the reduction of CO₂ to CO on Co-phthalocyanine. Subsequently, the CO molecule diffused to Zn-N-C and was further reduced to CH₄ on ZnN₄ through a pathway that involved the intermediate species *CH.

The electroreduction of CO₂ to C₂H₄ is a crucial and challenging undertaking due to its multi-electron nature. The production of C₂H₄ via electroreduction of CO₂ requires the transfer of 12 electrons, which is a significantly higher number of electrons compared to 2 electrons and 8 electrons required for the formation of CO/HCOOH and CH₄, respectively. Very recently, Qui et al. reported a highly selective reduction of CO₂ to C₂H₄ using a two-dimensional metal-organic framework constructed from phthalocyanine-Cu-(OH)₈ and CuO₄ nodes with Faradic efficiency for C₂H₄ production of 50% at -1.2 V_{RHE} (Table 1, Entry 7) [41]. They suggested that their two-dimensional structure could help to lower the energy barrier required for C-C dimerization, which is a vital step for CO₂ reduction to C₂H₄. The electrocatalytic reduction mechanism was suggested to involve a synergistic effect between the Cu-phthalocyanine and CuO₄ components [41]. The authors also studied their electrocatalysts after reaction using powder X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and X-ray photoelectron spectroscopy, as well as during catalysis by in-situ operando X-ray absorption spectroscopy, and claimed that no signals attributable to Cu(0) or changes in the Cu K-edges were apparent and that no evidence of Cu-Cu bonding could be seen in the X-ray absorption near-edge structure profiles. These data together were held to suggest that the Cu-phthalocyanine remained intact after catalysis.

3. Concluding remarks and future perspectives/challenges

This review gives an overview of reports of metal-phthalocyanine complexes as electrocatalysts for CO₂ reduction to products other than CO from recent years. Generally, metal-phthalocyanine complexes tend to produce CO as the main reaction product of carbon dioxide electro-reduction; however, as summarized here, there is an ever-growing body of reports where deeper reduction of CO₂ is evident. Creating an efficient metal-phthalocyanine catalyst for CO₂ reduction requires identifying reaction intermediates and pathways, and modifying the catalyst's chemical composition and structure to enhance electrochemical CO₂ reduction selectivity while inhibiting the competing hydrogen evolution

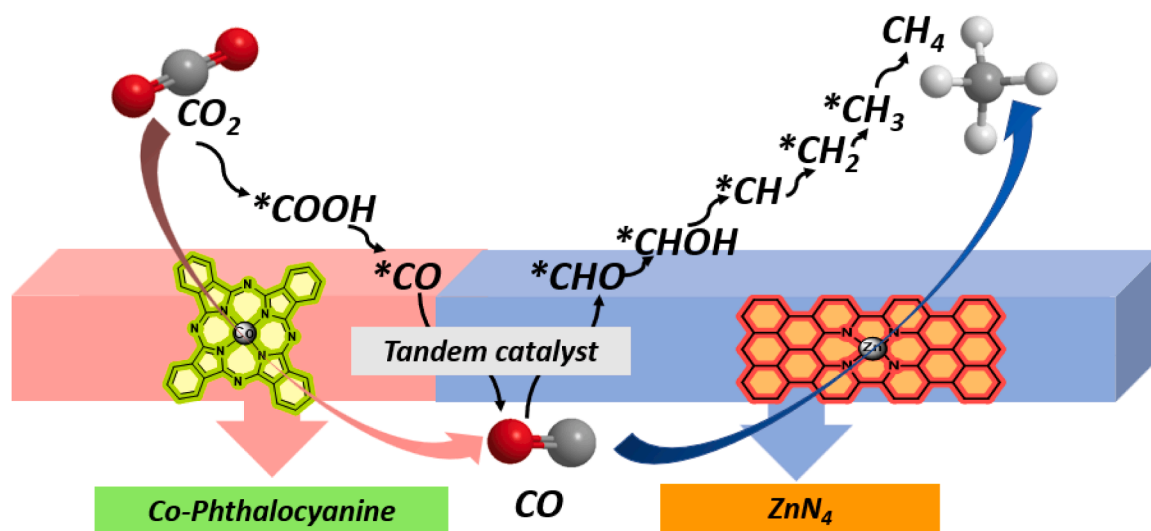


Fig. 7. A proposed reaction mechanism for electrochemical reduction of CO₂ to CH₄ over a tandem catalyst containing Co-phthalocyanine and zinc-nitrogen-carbon [54].

reaction. Co-phthalocyanine complexes are at the forefront in this regard.

However, there remains room for significant improvement. Amongst the strategies for increasing yields of non-CO products, modification of the ligand scaffold and tuning of the substrate support still offer considerable scope for exploration. For example, the low dispersibility and poor catalytic efficiency of metal-phthalocyanine complexes in water and common organic solvents limit their potential applications. By modification of ligands, the solubility of metal-phthalocyanines in organic solvents and aqueous solutions could be improved, which would improve their tractability and facilitate their use under a wider range of conditions. Likewise, direct immobilization of metal phthalocyanine molecules on electrodes can result in the formation of molecular aggregates, which in turn impairs catalytic performance for CO₂ reduction. Other challenges include the demetalation of the complexes during CO₂ reduction, leading to the formation of metal clusters that may be the active catalytic species [64–66]. Key factors affecting the formation of un-ligated metal species include the presence of CO₂ reduction intermediates, solution pH, temperature, catalyst dispersion on the electrode surface, the nature of the electrode support materials, and substrate surface properties. It is therefore essential that (as a minimum) analysis is performed on catalysts post-reaction in order to ascertain whether or not the original metal-phthalocyanine complexes are still intact, or if demetalation and formation of metal/metal-oxide clusters has occurred. Other challenges that remain include optimization of the interactions between the metal-phthalocyanine complexes and the substrate supports in order to enhance the catalytic activity of these molecules [22] and facilitate deeper CO₂ reduction [70], and scale-up from laboratory to demonstrator size (for example, by boosting electrode areas, current densities and Faradaic efficiencies) [71]. If these challenges can be overcome, then metal-phthalocyanine complexes could present a cost-effective and easily tunable class of electrocatalysts for the production of a range of valuable fuels and chemical feedstocks from carbon dioxide.

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.

Data Availability

No data was used for the research described in the article.

Acknowledgements

MDS thanks the Royal Society for a University Research Fellowship (URF\R\211007) and ZE thanks the Scientific and Technological Research Council of Turkey (grant number: TUBITAK 2219) for a post-doctoral fellowship. This work was supported by the EPSRC (EP/W033135/1).

References

- [1] S. Hernández, M.A. Farkhondehfar, F. Sastre, M. Makkee, G. Saracco, N. Russo, *Green. Chem.* 19 (2017) 2326–2346.
- [2] J. Fuhrman, C. Bergero, M. Weber, S. Monteith, F.M. Wang, A.F. Clarens, S. C. Doney, W. Shobe, H. McJeon, *Nat. Clim. Change* (2023) 1–10.
- [3] J. Rogelj, M. Den Elzen, N. Höhne, T. Fransen, H. Fekete, H. Winkler, R. Schaeffer, F. Sha, K. Riahi, M. Meinshausen, *Nature* 534 (2016) 631–639.
- [4] Y. Ou, G. Iyer, L. Clarke, J. Edmonds, A.A. Fawcett, N. Hultman, J.R. McFarland, M. Binsted, R. Cui, C. Fyson, A. Geiges, S. Gonzales-Zuniga, M.J. Gidden, N. Höhne, L. Jeffery, T. Kuramochi, J.L. Wis, M. Meinshausen, Z. Nicholls, P. Patel, S. Ragnaut, J. Rogelj, S. Waldhoff, S. Yu, H. McJeon, *Science* 374 (2021) 693–695.
- [5] M. Meinshausen, J. Lewis, C. McGlade, J. Gütschow, Z. Nicholls, R. Burdon, L. Cozzi, B. Hackmann, *Nature* 604 (2022) 304–309.
- [6] Z. Ma, Z. Yang, W. Lai, Q. Wang, Y. Qiao, H. Tao, C. Lian, M. Liu, C. Ma, A. Pan, H. Huang, *Nat. Commun.* 13 (2022) 7596.
- [7] I. Hussain, H. Alasiri, W.U. Khan, K. Alhooshani, *Coord. Chem. Rev.* 482 (2023), 215081.
- [8] F. He, S. Tong, Z. Luo, H. Ding, Z. Cheng, C. Li, Z. Qi, *J. Energy Chem.* (2023) 398–409.
- [9] T.M. Gür, *Prog. Energy Combust. Sci.* 89 (2022), 100965.
- [10] H.L.A. Dickinson, M.D. Symes, *Electrochem. Commun.* 135 (2022), 107212.
- [11] S. Nitopi, E. Bertheussen, S.B. Scott, X. Liu, A.K. Engstfeld, S. Horch, B. Seger, I. E. Stephens, K. Chan, C. Hahn, J.K. Norskov, T.F. Jaramillo, I. Chorkendorff, *Chem. Rev.* 119 (2019) 7610–7672.
- [12] F. Hussain, M.K. Aroua, *Rev. Chem. Eng.* 37 (2021) 863–884.
- [13] S. Garg, M. Li, A.Z. Weber, L. Ge, L. Li, V. Rudolph, G. Wang, T.E. Rufford, *J. Mater. Chem. A* 8 (2020) 1511–1544.
- [14] M. Jouny, W. Luc, F. Jiao, *Ind. Eng. Chem. Res.* 57 (2018) 2165–2177.
- [15] S. Overa, B.H. Ko, Y. Zhao, F. Jiao, *Acc. Chem. Res.* 55 (2022) 638–648.
- [16] G.F. Manbeck, E. Fujita, *J. Porphy. Phthalocyanines* 19 (2015) 45–64.
- [17] L. Zhang, Z.J. Zhao, J. Gong, *Angew. Chem. Int. Ed.* 56 (2017) 11326–11353.
- [18] X. Zhang, S.-X. Guo, K.A. Gandionco, A.M. Bond, J. Zhang, *Mater. Today Adv.* 7 (2020), 100074.
- [19] F. Yu, Z. Zhou, Y. You, J. Zhan, T. Yao, L.-H. Zhang, *ACS Appl. Mater. Interfaces* (2023) 24346–24353.
- [20] D.-D. Ma, S.-G. Han, C. Cao, X. Li, X.-T. Wu, Q.-L. Zhu, *Appl. Catal. B: Environ.* 264 (2020), 118530.
- [21] C. Yang, Z. Gao, D. Wang, S. Li, J. Li, Y. Zhu, H. Wang, W. Yang, X.J. Gao, Z. Zhang, *Sci. China Mater.* 65 (2022) 155–162.
- [22] Q. Feng, Y. Sun, X. Gu, Z. Dong, *Electrocatalysis* 13 (2022) 675–690.
- [23] N. Nandal, S.L. Jain, *Coord. Chem. Rev.* 451 (2022), 214271.
- [24] C.W. Li, J. Ciston, M.W. Kanan, *Nature* 508 (2014) 504–507.
- [25] H. Mistry, A.S. Varela, C.S. Bonifacio, I. Zegkinoglou, I. Sinev, Y.-W. Choi, K. Kisslinger, E.A. Stach, J.C. Yang, P. Strasser, B.R. Cuenya, *Nat. Commun.* 7 (2016) 12123.
- [26] A. Bagger, L. Arnarson, M.H. Hansen, E. Spohr, J. Rossmeisl, *J. Am. Chem. Soc.* 141 (2019) 1506–1514.
- [27] Y. Liu, F. Li, X. Zhang, X. Ji, *Curr. Opin. Green. Sustain. Chem.* 23 (2020) 10–17.
- [28] S. Yang, Y. Yu, X. Gao, Z. Zhang, F. Wang, *Chem. Soc. Rev.* 50 (2021) 12985–13011.
- [29] E. Boutin, M. Wang, J.C. Lin, M. Mesnage, D. Mendoza, B. Lassalle-Kaiser, C. Hahn, T.F. Jaramillo, M. Robert, *Angew. Chem. Int. Ed.* 58 (2019) 16172–16176.
- [30] Y. Wu, Y. Liang, H. Wang, *Acc. Chem. Res.* 54 (2021) 3149–3159.
- [31] A. Lever, *J. Porphy. Phthalocyanines* 3 (1999) 488–499.
- [32] Z. Yue, C. Ou, N. Ding, L. Tao, J. Zhao, J. Chen, *ChemCatChem* 12 (2020) 6103–6130.
- [33] P.K. Sonkar, V. Ganesan, R. Gupta, D.K. Yadav, M. Yadav, *J. Electroanal. Chem.* 826 (2018) 1–9.
- [34] C. Costentin, J.-M. Savéant, *Curr. Opin. Electrochem.* 1 (2017) 104–109.
- [35] X. Wang, Z.F. Cai, Y.Q. Wang, Y.C. Feng, H.J. Yan, D. Wang, L.J. Wan, *Angew. Chem. Int. Ed.* 59 (2020) 16098–16103.
- [36] S. Gong, W. Wang, R. Lu, M. Zhu, H. Wang, Y. Zhang, J. Xie, C. Wu, J. Liu, M. Li, S. Shao, G. Zhu, X. Lv, *Appl. Catal. B: Environ.* 318 (2022), 121813.
- [37] L. Sun, V. Reddu, A.C. Fisher, X. Wang, *Energy Environ. Sci.* 13 (2020) 374–403.
- [38] Q. Chang, Y. Liu, J.-H. Lee, D. Ologunagba, S. Hwang, Z. Xie, S. Kattel, J.H. Lee, J. G. Chen, *J. Am. Chem. Soc.* 144 (2022) 16131–16138.
- [39] N. Furuya, S. Koide, *Electrochim. Acta* 36 (1991) 1309–1313.
- [40] Y. Wu, J. Jiang, Z. Weng, M. Wang, D.L.L. Broere, Y. Zhong, G.W. Brudvig, Z. Feng, H. Wang, *ACS Cent. Sci.* 3 (2017) 847–852.
- [41] X.-F. Qiu, H.-L. Zhu, J.-R. Huang, P.-Q. Liao, X.-M. Chen, *J. Am. Chem. Soc.* 143 (2021) 7242–7246.
- [42] E. Boutin, A. Salamé, L. Merakeb, T. Chatterjee, M. Robert, *Chem. Eur. J.* 28 (2022), e202200697.
- [43] N.M. Latiff, X. Fu, D.K. Mohamed, A. Veksha, M. Handayani, G. Lisak, *Carbon* 168 (2020) 245–253.
- [44] X. Zhang, F. Li, J. Wang, H. Zhao, X.-F. Yu, *Appl. Energy* 298 (2021), 117196.
- [45] P. Tian, B. Zhang, J. Chen, J. Zhang, L. Huang, R. Ye, B. Bao, M. Zhu, *Catal. Sci. Technol.* 11 (2021) 2491–2496.
- [46] Q. Wan, Q. He, Y. Zhang, L. Zhang, J. Li, J. Hou, X. Zhuang, C. Ke, J. Zhang, *Electrochim. Acta* 392 (2021), 139023.
- [47] J. Shen, R. Kortlever, R. Kas, Y.Y. Birdja, O. Diaz-Morales, Y. Kwon, I. Ledezma-Yanez, K.J.P. Schouten, G. Mul, M.T. Koper, *Nat. Commun.* 6 (2015) 8177.
- [48] T. Abe, F. Taguchi, T. Yoshida, S. Tokita, G. Schnurpfeil, D. Wöhrle, M. Kaneko, *J. Mol. Catal. A: Chem.* 112 (1996) 55–61.
- [49] Y. Wu, Z. Jiang, X. Lu, Y. Liang, H. Wang, *Nature* 575 (2019) 639–642.
- [50] X. Zhang, Y. Wang, M. Gu, M. Wang, Z. Zhang, W. Pan, Z. Jiang, H. Zheng, M. Lucero, H. Wang, G.E. Sterbinsky, Q. Ma, Y.-G. Wang, Z. Feng, J. Li, H. Dai, Y. Liang, *Nat. Energy* 5 (2020) 684–692.
- [51] J. Zheng, X. Li, Y. Qin, S. Zhang, M. Sun, X. Duan, H. Sun, P. Li, S. Wang, *J. Catal.* 371 (2019) 214–223.
- [52] R. Wang, E. Boutin, N. Barreau, F. Odobel, J. Bonin, M. Robert, *ChemPhotoChem* 5 (2021) 705–710.
- [53] Q. Zhao, Y. Wang, S. Zhu, E.P. Delmo, Y. Cui, T. Lin, R.C. Dutta, J. Li, F. Xiao, T. Li, R.C. Dutta, J. Li, F. Xiao, T. Li, Y. Wang, J. Jang, Q. Wei, G. Chen, M. Shao, *J. Phys. Chem. C* 126 (2022) 17502–17509.
- [54] L. Lin, T. Liu, J. Xiao, H. Li, P. Wei, D. Gao, B. Nan, R. Si, G. Wang, X. Bao, *Angew. Chem. Int. Ed.* 59 (2020) 22408–22413.
- [55] M. Li, T. Li, R. Wang, C. Sun, N. Zhang, R. Gao, Y. Song, *Chem. Commun.* 58 (2022) 12192–12195.
- [56] S. Acharjya, J. Chen, M. Zhu, C. Peng, *Greenh. Gases: Sci. Technol.* 11 (2021) 1191–1197.

- [57] J. Bian, L. Sun, Z. Zhang, Z. Li, M. Chu, X. Li, D. Tang, L. Jing, *ACS Sustain. Chem. Eng.* 9 (2021) 2400–2408.
- [58] R. Sun, Y. Wang, Z. Zhang, Y. Qu, Z. Li, B. Li, H. Wu, X. Hua, S. Zhang, F. Zhang, L. Jing, *Chem. Eng. J.* 426 (2021), 131266.
- [59] S. Kang, Z. Li, Z. Xu, Z. Zhang, J. Sun, J. Bian, L. Bai, Y. Qu, L. Jing, *Catal. Sci. Technol.* 12 (2022) 4817–4825.
- [60] X.F. Qiu, J.R. Huang, C. Yu, Z.H. Zhao, H.L. Zhu, Z. Ke, P.Q. Liao, X.M. Chen, *Angew. Chem. Int. Ed.* 61 (2022), e202206470.
- [61] N. Nandal, N.R. Manwar, B.M. Abraham, P.K. Khatri, S.L. Jain, *Energy Fuels* 36 (2022) 3760–3770.
- [62] S. Singh, M.T. Noori, N. Verma, *Electrochim. Acta* 338 (2020), 135887.
- [63] Z. Ji, K.W. Wong, M. Wang, P. Ken, R. Kwok, W. Lau, *Nucl. Instrum. Methods Phys. Res. Sect. B: Beam Interact. Mater. At.* 174 (2001) 311–316.
- [64] S. Ren, Z. Zhang, E.W. Lees, A.G. Fink, L. Melo, C. Hunt, D.J. Dvorak, W.Y. Wu, E. R. Grant, C.P. Berlinguette, *Chem. Eur. J.* 28 (2022), e202200340.
- [65] Z. Weng, Y. Wu, M. Wang, J. Jiang, K. Yang, S. Huo, X.-F. Wang, Q. Ma, G. W. Brudvig, V.S. Batista, Z. Feng, H. Wang, *Nat. Commun.* 9 (2018) 415.
- [66] J. Zhang, T.H. My Pham, Z. Gao, M. Li, Y. Ko, L. Lombardo, W. Zhao, W. Luo, A. Züttel, *ACS Catal.* 13 (2023) 9326–9335.
- [67] X. Lyu, J. Li, T. Zhang, Z. Li, I.-H. Hwang, C. Sun, C.J. Jafra, J. Yang, T.J. Toops, D. A. Cullen, A. Serov, J. Wu, *EES Catal.* 1 (2023) 117–124.
- [68] C. Yan, H. Li, Y. Ye, H. Wu, F. Cai, R. Si, J. Xiao, S. Miao, S. Xie, F. Yang, Y. Li, G. Wang, X. Bao, *Energy Environ. Sci.* 11 (2018) 1204–1210.
- [69] Z. Zhang, H. Yin, G. Yu, S. He, J. Kang, Z. Liu, K. Cheng, Q. Zhang, Y. Wang, *J. Catal.* 395 (2021) 350–361.
- [70] H.-L. Zhu, L. Zhang, M. Shui, Z.-Y. Li, J.-J. Ma, Y.-Q. Zheng, *J. Phys. Chem. Lett.* 14 (2023) 3844–3852.
- [71] X. Wu, J.W. Sun, P.F. Liu, J.Y. Zhao, Y. Liu, L. Guo, S. Dai, H.G. Yang, H. Zhao, *Adv. Funct. Mater.* 32 (2022) 2107301.