# The Role of Undercoordinated Sites on Zinc Electrodes for CO<sub>2</sub> Reduction to CO

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The electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) using renewable energies is a promising route toward global carbon neutrality. Recently, the use of copper catalysts and CO feedstocks, instead of CO<sub>2</sub>, has been shown to enhance the selectivity toward multicarbon products, leading to increased efforts in developing tandem electrocatalytic systems. State-of-the-art CO<sub>2</sub>-to-CO electrocatalysts are mainly based on noble metals such as silver and gold. Earth-abundant zinc, in contrast, displays poorer selectivity and activity. Herein, the use of porous dendritic oxidederived zinc (OD-Zn) catalysts for CO<sub>2</sub>RR is reported. These catalysts can reduce CO<sub>2</sub> to CO with a maximum Faradaic efficiency of 86% at -0.95 V versus reversible hydrogen electrode (RHE) and partial current density of -266 mA cm<sup>-2</sup> at -1.00 V vs RHE. OD-Zn is further found to have a higher amount of undercoordinated sites and exhibits higher CO<sub>2</sub>RR activity and CO selectivity than electrodeposited Zn metal. While oxygen vacancies have been previously implicated as active sites, detailed experiments and density functional theory calculations show that Zn sites with a high degree of undercoordination provide even higher activity, in view of their nearly optimal \*COOH adsorption energies. These findings showcase Zn-Oderived particles with plentiful undercoordinated sites as cost-effective electrocatalysts for CO production.

## 1. Introduction

The world depends greatly on fossil fuels and their derivatives, such as CO and  $H_2$ , to produce a wide variety of commodity

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chemicals.<sup>[1]</sup> As fossil fuels are a finite resource, and their extraction and usage are closely associated with major environmental issues such as groundwater pollution and imbalances in the carbon cycle, it is vital to replace them with a more sustainable resource. One such resource is CO<sub>2</sub>, the most thermodynamically stable form of carbon.<sup>[2]</sup> Using renewable electricity and a suitable catalyst such as copper, the electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) has been shown to be a potentially sustainable approach to produce high-value fuels and commodity chemicals, such as methane, ethanol, and ethylene.<sup>[3,4]</sup>

Nevertheless, the selectivity and energetic efficiency of  $CO_2RR$  processes are currently far from optimal. For example, 1-propanol, a  $C_3$  oxygenate, can only be produced with modest Faradaic efficiencies (FEs) below 15%, even when large overpotentials close to 1 V are applied.<sup>[5]</sup> One reason for this dismal performance is that the electrocatalysts used for producing the necessary CO intermediates from  $CO_2$ , and for reducing the CO to hydro-

carbons/oxygenates are essentially different.<sup>[6]</sup> The former, which consists mainly of Ag, Au, and Zn, binds CO weakly, while the latter (only Cu among the pure metals) binds CO with intermediate bond strength. Thus, while the former metals are suitable for reducing CO<sub>2</sub> to CO,<sup>[7]</sup> they are unable to bind CO strongly enough so as to catalyze its further hydrogenation and/or subsequent C–C coupling required to form multicarbon products. From this perspective, it is more apt to devise a tandem process where CO<sub>2</sub> is first converted to CO, and then engineer functional catalysts for the reduction of CO to the target products. Similar to CO<sub>2</sub>, CO can react in a multifurcated way to give multicarbon oxygenates and hydrocarbons, albeit with higher selectivity, activity, and energetic efficiency.<sup>[8,9]</sup>

Technoeconomic analyses have shown that CO can be produced from  $CO_2RR$  cost-effectively, due to the low number of electrons (two) required to form each molecule and the resulting high product value per electron.<sup>[10,11]</sup> Solid-oxide electrolysis cells have been commercialized for this purpose, and operate at current densities exceeding -750 mA cm<sup>-2</sup>, with 100% FE for CO (FE<sub>CO</sub>).<sup>[12]</sup> However, these devices are energy-intensive because their operational temperatures are in the range of 700–900 °C. Therefore, low-temperature electrolysis has been explored for CO production. Ag- and Au-based catalysts can convert CO<sub>2</sub>

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Table 1. Summary of  $\mathsf{CO}_2\mathsf{RR}$  to CO performance on Ag-, Au-, and Zn-based electrocatalysts.

#### Table 1. Continued.

Catalyst <sup>a)</sup>	Experimental Conditions	FE <sub>CO</sub>	İco	Stability
	· · · · · · · · · ·		[mA cm <sup>-2</sup> ]	
Oxide-derived Zn dendrites; OD-Zn <sub>2.5</sub>	Flow cell 2 м КНСО3 –1.00 V vs RHE	80.3%	-266	_
(this work)	Flow cell 2 м КНСО <sub>3</sub> –0.95 V vs RHE	84.8%	-171	6 h
Sharp-tipped Zn nanowires <sup>[25]</sup>	H-cell 0.5 м КНСО <sub>3</sub> –0.95 V vs RHE	98%	-39.2	35 h
Electrodeposited Zn dendrites <sup>[26]</sup>	H-cell 0.5 м NaHCO₃ –1.1 V vs RHE	79%	-14	3 h
ZnO nanosheets with oxygen vacancies <sup>[27]</sup>	H-cell 0.1 м КНСО₃ −1.1 V vs RHE	83%	-16.1	8 h
Oxide-derived multilayered Zn nanosheets <sup>[28]</sup>	H-cell 0.5 м NaHCO₃ –1.13 V vs RHE	86%	-5.2	7 h
Oxide-derived Zn nanosheets <sup>[29]</sup>	H-cell 0.1 м КНСО <sub>3</sub> –1.0 V vs RHE	90%	≈–7.2	12 h
Oxide-derived Zn nanoplates <sup>[30]</sup>	H-cell 0.5 м NaCl –1.6 V vs SCE	93%	≈–14.0	10 h
Reduced nanopo- rous ZnO <sup>[31]</sup>	H-cell 0.25 м K₂SO₄ −1.66 V vs Ag/AgCl	92%	-15.1	_
Porous Zn network <sup>[32]</sup>	H-cell 0.5 м КНСО₃ –1.1 V vs RHE	80%	-16	-
Electrodeposited Zn on Cu mesh <sup>[33]</sup>	Flow cell 1 м КОН Chronopotentiometry: -200 mA cm <sup>-2</sup>	84%	-168	-
	Flow cell 1 м КОН –0.55 V vs RHE	≈56.5% <sup>b)</sup>	≈-42.4 <sup>c)</sup>	6 h
Reduced ZnO NPs <sup>[34]</sup>	Flow cell 1 м КОН Chronopotentiometry: -200 mA cm <sup>-2</sup>	91.6%	-183	_
	Flow cell 1 м КОН Chronopotentiometry: -500 mA cm <sup>-2</sup>	77.6%	-388	_
	Flow cell 1 м КОН Chronopotentiometry: –100 mA cm <sup>-2</sup>	≈90% <sup>d)</sup>	≈–90	3 h
Au NPs supported on PyPBI-wrapped MWNTs <sup>e),[7]</sup>	Flow cell 2 м КОН -0.44 V vs RHE	≈90%	≈-96.3 <sup>f)</sup>	8 h
Au nanoclusters <sup>[13]</sup>	Flow cell 3 м КОН –0.56 V vs RHE	≈90%	-230	_

Catalyst <sup>a)</sup>	Experimental Conditions	FE <sub>CO</sub>	j <sub>co</sub> [mA cm <sup>-2</sup> ]	Stability
Au/C electrodes <sup>[14]</sup>	Gas-phase-connected H-type cell 1 м КОН Chronopotentiometry: –100 mA cm <sup>-2</sup>	≈87.5% <sup>g)</sup>	≈-87.5	10 h
Ag NPs with PSTMIM <sup>h)</sup> ionomer <sup>[15]</sup>	Membrane electrode assembly 10 mм КНСО <sub>3</sub> Chronopotentiometry: –200 mA cm <sup>-2</sup>	≈98%	≈–196	1000 h
Sputtered Ag/PTFE <sup>[16]</sup>	Flow cell 1 м КОН –0.7 V vs RHE	≈90%	≈–144 <sup>i)</sup>	100 h
Ag GDE <sup>[17]</sup>	Zero-gap flow cell Mixture of 0.4 m K <sub>2</sub> SO <sub>4</sub> and 0.5 m KHCO <sub>3</sub> Chronopotentiometry: -300 mA cm <sup>-2</sup>	≈65%	≈–195	1200 h
Ag NPs <sup>[18]</sup>	Flow cell 1 м КОН –2.2 V vs Ag/AgCl	≈ <b>97.4%</b>	≈–280	-
Ag NPs on MWCNTs <sup>j),[19]</sup>	Flow cell 1 м КОН –0.8 V vs RHE	≈100%	-350	_
Ag GDEs <sup>[20]</sup>	Flow cell 0.5 м K <sub>2</sub> SO <sub>4</sub> Chronopotentiometry: –150 mA cm <sup>-2</sup>	≈70% <sup>k)</sup>	≈–105	800 h
Sputtered Ag <sup>[21]</sup>	Flow cell, 7 atm 7 м КОН Chronopotentiometry: –300 mA cm <sup>-2</sup>	≈100%	≈–300	_
Ag coordination polymer <sup>[22]</sup>	Flow cell 1 м КОН Chronopotentiometry: -400 mA cm <sup>-2</sup>	96.3%	-385	-

<sup>a)</sup>The numbers containing "≈" in this table are estimated from the corresponding literature as the values were not provided. For the Au- and Ag-based catalysts, only literature data using flow cells are included for fairer comparison of the catalysts; <sup>b)</sup>The FE<sub>CO</sub> fluctuated between 55% and 58%; an average of 56.5% was used to determine  $j_{CO}$ ; <sup>c)</sup>The  $j_{total}$  fluctuated between -60 and -90 mA cm<sup>-2</sup>, an average of 90% was used to determine  $j_{CO}$ ; <sup>e)</sup>Au nanoparticles supported on poly(2,2'-(2,6-pyridine)-5,5'-bibenzimidazole) polymer (PyPBI) wrapped multiwall carbon nanotubes (MWNTs); <sup>f)</sup>The  $j_{total}$  decreased from ≈–111 to ≈–103 mA cm<sup>-2</sup> over 8 h electrolysis; an average  $j_{total}$  of -107 mA cm<sup>-2</sup> was used to determine  $j_{CO}$ ; <sup>f)</sup>Polystyrene tetramethyl methylimidazolium chloride (PSTMIN); <sup>f)</sup>The  $j_{total}$  fluctuated between 83% and 92%; an average of 87.5% was used to determine  $j_{CO}$ ; <sup>f)</sup>Pholystyrene tetramethyl methylimidazoli (MWCNTs); <sup>f)</sup>The  $f_{total}$  fluctuated between 60 and -170 mA cm<sup>-2</sup>; an average of -160 mA cm<sup>-2</sup> was used to determine  $j_{CO}$ ; <sup>f)</sup>Pholystyrene tetramethyl methylimidazoli (MWCNTs); <sup>f)</sup>The  $F_{CO}$  fluctuated between -150 and -170 mA cm<sup>-2</sup>; an average of -160 mA cm<sup>-2</sup> was used to determine  $j_{CO}$ ; <sup>h)</sup>Multiwalled carbon nanotubes (MWCNTs); <sup>k)</sup>The FE<sub>CO</sub> fluctuated between 60% and 80%; an average of 70% was used to determine  $j_{CO}$ .

to CO with FEs of 70–100% and CO current densities ( $j_{CO}$ ) of –88 to –385 mA cm<sup>-2</sup>.<sup>[7,13–22]</sup> Nonetheless, noble metals are costly (cost per kg in August 2021: Au [99.9% purity] = USD 57400; Ag [99.5%] = USD 770),<sup>[23]</sup> and many cannot sustain CO production with industrially relevant selectivity and activity (**Table 1**).

As an alternative, Zn is earth-abundant—at least 17 000 and 900 times more abundant than Au and Ag, respectively.<sup>[24]</sup> It is also cheaper than Ag and Au (Zn [99.995%]: USD 3 per kg as of August 2021).<sup>[23]</sup> This makes its deployment for industrial-scale  $CO_2$  electrolysis more economically viable. The drawback of using Zn, in particular, planar Zn electrodes, is their low selectivity toward CO. Interestingly, this can be increased beyond 90% by using Zn nanostructures such as nanowires,<sup>[25]</sup> dendrites,<sup>[26]</sup> nanosheets,<sup>[27–29]</sup> nanoplates,<sup>[30]</sup> and porous structures.<sup>[31–33]</sup> Recently, Züttel and coworkers also demonstrated high  $j_{CO}$  of -168 and -188 mA cm<sup>-2</sup> using gas diffusion electrodes (GDEs) loaded with porous Zn and oxide-derived Zn, respectively.<sup>[33,34]</sup> The high activities of the electrodes have been attributed to their large electrochemically active surface areas.<sup>[25,26,28,32,33]</sup>

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To fabricate catalysts with high surface areas, metal oxides such as those based on Au,  $^{[35]}\mbox{Ag}, ^{[36]}\mbox{ and }\mbox{Cu}^{[37]}\mbox{ have been used}$ as they can undergo dissolution and redeposition during CO<sub>2</sub>RR, vielding roughened structures. These oxide-derived catalysts have been shown to give enhanced CO activity and selectivity.<sup>[27-31,34,36]</sup> They have also been suggested to be rich in defects, such as undercoordinated metal atoms, which are commonly regarded by the research community as the active sites.<sup>[38]</sup> Nonetheless, we highlight that previous works have also shown that electrocatalytically active sites are not always located at defects. For example, the (100) facet of several transition metals has been found active for different electrocatalytic reactions by virtue of ensemble effects.<sup>[39-41]</sup> For Zn-based catalysts, Zeng et al. have further proposed that oxygen vacancies in ZnO-derived catalysts might be the active sites for CO<sub>2</sub> reduction to CO.<sup>[27]</sup> On the other hand, other authors suspected edge sites to be active.<sup>[28]</sup> These results cast doubt on the true nature of the active sites on Zn for CO production. As such, its chemical state (metallic versus oxidized) and optimal coordination environment ought to be explored.

Herein, we fabricate porous Zn catalysts (OD-Zn) derived in situ from ZnO nanoparticles (NPs) during CO2 electrolysis, and probe the origin of their functionality for producing CO. We first determined, through spectroscopic characterization, that there is a larger amount of undercoordinated sites on OD-Zn, as compared to on electrodeposited metallic Zn (ED-Zn). We further found linear correlations between  $j_{CO}$  and the roughness factors of the OD-Zn and ED-Zn electrodes. Interestingly, the correlation between the  $i_{CO}$ -roughness factor of ED-Zn was different from that of OD-Zn. For ED-Zn and OD-Zn samples with similar roughness factors, the activity of ED-Zn was dramatically lower. This indicates that the electrode surface area is not the sole factor influencing the conversion of CO<sub>2</sub> to CO. Instead, by means of detailed density functional theory (DFT) and coordination-activity plots, we found that among the various possible catalytic sites on OD-Zn, it is the highly undercoordinated Zn sites, and not oxygen vacancies as previously suggested, that catalyze CO<sub>2</sub> reduction to CO at significantly lower onset potentials. The efficacy of highly undercoordinated sites is attributed to their nearly optimal adsorption energies of \*COOH.

#### 2. Results and Discussion

#### 2.1. Catalyst Characterization

We synthesized ZnO NPs using a previously reported method (Section S1.1, Supporting Information).<sup>[42]</sup> Transmission and

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scanning electron microscopy (TEM and SEM) showed that the ZnO NPs were 20–50 nm in size (**Figure 1a**). High-resolution TEM revealed the presence of ZnO(100) planes with their characteristic lattice spacings of 0.28 nm (Figure S3a, Supporting Information).

Electrodeposited Zn GDEs (ED-Zn) were also prepared (Section S1.2, Supporting Information). ED-Zn<sub>10 min</sub> was in the form of hexagonal plates 5  $\mu$ m in size (Figure 1b; the duration of the electrodeposition [10 min] is reflected in the subscript). Selected area electron diffraction indicated that ED-Zn consisted of metallic Zn (Figure S3b, Supporting Information). In addition, commercially available ZnO particles (S-ZnO and M-ZnO) were used to compare the CO<sub>2</sub>RR performance of particles with different morphologies and sizes. The two samples consisted of nanoparticles and nanorods with sizes of 30–200 and 120–410 nm, respectively (Figure S3c–f, Supporting Information).

The synthesized ZnO NPs were loaded  $(0.25-3.25 \text{ mg cm}^{-2})$ onto carbon gas diffusion layers (GDL), and used for CO<sub>2</sub>RR in a flow cell (Section S1.4, Supporting Information). These electrodes are herein referred to as OD-Zn<sub>a</sub>, with the ZnO mass loadings "a" reflected in subscripts. Aqueous 2 м КНСО3 (pH  $\approx$  9.02) was used as electrolyte. Electrodes loaded with 2.5 mg cm<sup>-2</sup> of S-ZnO and M-ZnO were similarly prepared. CO<sub>2</sub>RR was performed at a representative potential of -0.95 V versus reversible hydrogen electrode (RHE; all potentials cited hereafter are referenced to the RHE). After CO<sub>2</sub>RR, all catalysts were observed to have transformed into porous, dendritic structures (Figure 1c,d and Figure S4, Supporting Information), which were likely formed via a dissolutiondeposition process.<sup>[43]</sup> Note that at the current densities typically attained on GDEs during electrolysis, the pH on the surface of the electrode is expected to be higher than that of the bulk electrolyte (a local pH of 11.9 was simulated when a current of  $-50 \text{ mA cm}^{-2}$  was applied to a GDE model in 1 M KHCO<sub>3</sub> electrolyte).<sup>[44]</sup> Therefore, even metallic Zn can dissolve in the electrolyte due to the elevated concentrations of OH- ions. The porous structures can be attributed to the evolution of hydrogen gas bubbles as the dendrites are formed.<sup>[45]</sup> The dendrites became more branched-out and thinner as the mass loading of ZnO NPs increased from 0.5 to  $3.25 \text{ mg cm}^{-2}$  (the width of the dendrites decreased from  $158 \pm 30$  to  $46 \pm 16$  nm; Figure S5, Supporting Information).

The chemical compositions of pristine ZnO NPs, S-ZnO, and M-ZnO were investigated using X-ray diffraction (XRD, Figure 1e and Figure S6, Supporting Information). These catalysts showed peaks corresponding to ZnO. After being used as CO<sub>2</sub>RR catalysts at -0.95 V, the major peaks measured can be ascribed to metallic Zn. The reduction of ZnO to metallic Zn is consistent with the reducing conditions used for CO<sub>2</sub>RR, and is in line with predictions from the Pourbaix diagram of the Zn-H<sub>2</sub>O system (at pH 9.02, reduction occurs at -0.97 V vs standard hydrogen electrode, or -0.44 V vs RHE).<sup>[46]</sup> It also agrees with previous works showing Zn oxides being reduced to metallic Zn during CO<sub>2</sub>RR.<sup>[29-31]</sup> The minor peaks in the XRD can be assigned to ZnO, likely due to Zn oxidation by atmospheric oxygen during sample transfer for XRD analysis.<sup>[47]</sup> We cannot, though, exclude the possibility that these may arise due to the incomplete reduction of all the ZnO to metallic Zn during electrolysis. For ED-Zn, only XRD peaks from metallic





**Figure 1.** SEM images of a) ZnO NPs and b) ED-Zn<sub>10min</sub> before these were used as catalysts for  $CO_2RR$ . SEM images of c) OD-Zn<sub>2.5</sub> and d) ED-Zn<sub>10min</sub> after they were used as catalysts for  $CO_2RR$ . The corresponding TEM images are shown in the insets. e) XRD patterns of OD-Zn and ED-Zn before and after  $CO_2RR$ . XRD patterns of Zn and ZnO standards are included. Peaks from the GDL are marked using asterisks (\*). f) Operando Raman spectra of OD-Zn obtained at various timings during  $CO_2$  electrolysis at -0.95 V. The timings are indicated by the numbers on the right of each spectrum. g) Ex situ Raman spectra of OD-Zn before and after  $CO_2RR$ . h[i] Zn LMM Auger spectra of ED-Zn and OD-Zn after  $CO_2RR$ . The XPS Zn 2p spectra were not used for analysis due to the difficulty in differentiating between the Zn<sup>0</sup> and Zn<sup>2+</sup> peaks. h[ii] XPS O 1s spectra of ED-Zn and OD-Zn after  $CO_2RR$ . The values in black-colored fonts are the relative areas (in percentages) of the fitted curves. All  $CO_2$  electrolysis experiments were performed at -0.95 V.

Zn were recorded before and after  $CO_2RR$  (Figure 1e). However, similar to OD-Zn, we can expect small amounts of Zn oxide to be present due to the rapid oxidation of the Zn surface under ambient conditions. Overall, from their SEM images and XRD patterns, both OD-Zn and ED-Zn appeared similar in terms of morphology and chemical composition, after they were used for  $CO_2RR$ .

The coordination of the Zn sites in the two catalysts was further probed by in- and ex situ Raman spectroscopy. Measurements were made on catalysts deposited on Zn disk substrates as proxies to the Zn GDEs (to minimize signal interferences from carbon; see Section S1.2, Supporting Information). At opencircuit potential, the Raman spectrum of OD-Zn comprised peaks which can be assigned to ZnO (Figure 1f).<sup>[48]</sup> When the catalyst was biased at -0.95 V, operando Raman spectroscopy showed that these peaks became nondetectable within 195 s. We attribute this to the reduction of ZnO to metallic Zn during CO<sub>2</sub>RR (consistent with the XRD data in Figure 1e), which can also be observed from the oxide reduction peaks of chronoamperograms recorded during CO<sub>2</sub> electrolysis

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(Figure S7, Supporting Information). No peaks due to the \*COOH and \*CO adsorbates were recorded. This is likely due to the insufficient limits of detection of our Raman spectrometer, as well as the short lifetimes of these adsorbates on Zn.

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Comparing the ex situ Raman spectra of OD-Zn before and after  $CO_2$  reduction, we observe that the ZnO  $E_2^{high}$  phonon mode shifts from 436 to 426 cm<sup>-1</sup> (Figure 1g; the  $E_2^{high}$  mode involves O atoms moving in opposite directions while the Zn sublattice is stationary.<sup>[48]</sup>) This shift can be ascribed to the presence of oxygen vacancies in OD-Zn: the oxygen vacancies result in lower amounts of movements of O atoms, leading to a redshift in the E2<sup>high</sup> mode.<sup>[49,50]</sup> In contrast, no Raman peaks could be measured on ED-Zn (Figure S8, Supporting Information), which indicates that ED-Zn is more metallic than OD-Zn.

Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) (ex situ analytical methods) were further performed to quantify the oxygen vacancies (Sections S1.2 and S1.3, Supporting Information). The Zn LMM Auger spectra of OD-Zn and ED-Zn after they were used for CO<sub>2</sub>RR (Figure 1h[i]) comprised ZnO peaks (986 and 989 eV) and Zn peaks (992 and 996 eV),<sup>[51]</sup> which indicate that surface oxides were present on both catalysts. The O 1s XPS spectra of the catalysts could be deconvoluted into two peaks at 530.3 and 531.5 eV (Figure 1h[ii]). These correspond, respectively, to oxygen in Zn-O bonding and oxygen in oxygen-deficient regions within the ZnO matrix.<sup>[52]</sup> After CO<sub>2</sub>RR, the ratio of oxygen surrounding oxygen vacancies to oxygen in O-Zn bonding in OD-Zn (≈3.3) was considerably higher than that of ED-Zn (≈1.6).

We interpret the above observations as follows. The ZnO NPs were reduced mainly to metallic Zn under negative potentials (Figure 1f). Metallic Zn atoms are, thus, likely to form the catalytic active sites. After the completion of CO<sub>2</sub>RR, the Zn surfaces re-oxidized in the ambient environment. Re-oxidized OD-Zn was found to contain a relatively higher concentration of oxygen vacancies, as compared to the re-oxidized ED-Zn (Figure 1g,h[ii]). We attribute this to the larger population of undercoordinated Zn sites on OD-Zn, which have a greater propensity to oxidize (post-CO<sub>2</sub>RR) to ZnO with more oxygen vacancies. In line with this, recent works have noted the formation of oxygen vacancies on amorphous and roughened TiO<sub>2</sub>, but not on highly crystalline TiO<sub>2</sub> particles.<sup>[53]</sup> Previous studies

have also suggested that undercoordinated sites are present in oxide-derived metal catalysts.<sup>[8,37,38,54]</sup> DFT calculations will also be used later in Section 2.3 to provide a firmer theoretical basis for this interpretation.

#### 2.2. Correlation between CO<sub>2</sub>RR Activity and Surface Areas of **OD-Zn and ED-Zn**

The effect of applied potentials on CO<sub>2</sub>RR was first investigated on OD-Zn with a mass loading of 2.5 mg cm<sup>-2</sup> (OD-Zn<sub>2.5</sub>). Its onset potential for CO production was -0.40 V. The FE<sub>CO</sub> increases as the applied potential increases, with FEs of 69-86% over a potential range of -0.85 to -1.05 V (Figure 2a). Formate is a minor carbonaceous product with FE < 1%. The maximum FE<sub>CO</sub> and  $j_{CO}$  were 86% at -0.95 V and -266 mA cm<sup>-2</sup> at -1.00 V, respectively. The catalyst was stable for at least 6 h during CO<sub>2</sub>RR at -0.95 V, with an average FE<sub>CO</sub> of 85%, and  $j_{CO}$  of -171 mA cm<sup>-2</sup> (Figure 2b). It is notable that the FE<sub>CO</sub> achieved at all investigated potentials on OD-Zn<sub>25</sub> were 9-26 FE % units higher than a previous study of CO<sub>2</sub>RR using porous Zn GDEs in KHCO3 electrolyte, which attained 60%  $FE_{CO}$  with  $j_{CO}$  of -180 mA cm<sup>-2</sup> at -0.95 V (Table 1).<sup>[33]</sup>

Using the potential which gave the highest  $FE_{CO}$  (-0.95 V), we investigated the CO<sub>2</sub>RR activity of all the OD-Zn and ED-Zn electrodes. The roughness factors of the electrodes were also estimated using the total charge density of the Zn<sup>0</sup> to Zn<sup>2+</sup> oxidation peak at -0.01 V in their cyclic voltammograms (measured after CO<sub>2</sub>RR. Figure S9a and Section S1.3, Supporting Information).<sup>[55]</sup> We found that  $j_{CO}$  and the roughness factor of the OD-Zn electrodes were correlated positively (Figure 3). The roughness factors of the OD-Zn electrodes increased from 42 to 929 when the ZnO NPs mass loading increased from 0.5 to 2.5 mg cm<sup>-2</sup>. For the same range of catalyst loadings,  $j_{\rm CO}$  increased from –48 to –201 mA  $\rm cm^{-2}$ (Figure S10a, Supporting Information), with the highest  $j_{CO}$ exhibited by OD-Zn $_{2.5}.$  The  $\ensuremath{\text{FE}_{\text{CO}}}$  increased from 79% (for OD-Zn<sub>0.5</sub>) to 92% (OD-Zn<sub>1.25</sub>), before decreasing to 86% (OD-Zn<sub>25</sub>). The decrease in  $FE_{CO}$  at high mass loading could stem from the thicker catalyst layer, which resulted in poor diffusion of CO<sub>2</sub> within the catalyst layer and, therefore, relatively higher H<sub>2</sub> production.



Figure 2. a) Faradaic efficiencies of CO and H<sub>2</sub>, and partial current densities of CO obtained using OD-Zn<sub>2.5</sub> from -0.85 to -1.05 V. b) Long-term performance of OD-Zn<sub>2.5</sub> at -0.95 V.





**Figure 3.** Correlation between the surface roughness factors of the electrodes and  $j_{CO}$  achieved with different mass loadings of ZnO NPs (OD-Zn), commercial ZnO particles, and ED-Zn (duration of electrodeposition from 30 s to 20 min). The CO<sub>2</sub> electrolysis experiments were performed at -0.95 V. The dashed lines are added as a guide to the eye. *R* represents the correlation coefficient between  $-j_{CO}$  and roughness factor.

When the mass loading was further increased to 3.25 mg cm<sup>-2</sup>, the roughness factor decreased to 803, while both  $FE_{CO}$  and  $j_{CO}$  decreased to 73% and -169 mA cm<sup>-2</sup>, respectively (Figure 3 and Figure S10a, Supporting Information). We attribute the decrease in roughness factor to excessive particle agglomeration, which will lower the amount of available active sites. The current densities and FEs of CO achieved using OD-Zn<sub>2.5</sub> is comparable to state-of-the-art Ag-based catalysts (Table 1). Furthermore, the CO<sub>2</sub>RR activities of electrodes prepared from ZnO (including S-ZnO and M-ZnO) correlate positively to their roughness factors (Figure 3).

 $CO_2$  electrolysis was performed on ED-Zn electrodes (the onset potential for CO evolution on ED-Zn<sub>10 min</sub> was -0.40 V). Interestingly, the plot of  $j_{CO}$  versus roughness factor of the ED-Zn electrodes displayed a linear fit with a gentler slope (0.023) as compared to that of OD-Zn (0.19). Their FE<sub>CO</sub> (56–68%) and  $j_{CO}$  (17–34 mA cm<sup>-2</sup>) were also lower than those of the OD-Zn electrodes (Figure 3 inset and Figure S10b, Supporting Information). This suggests that apart from the surface areas of the electrodes, the coordination of the Zn sites could have influenced the CO selectivity and activity. Further insights will be provided by DFT calculations in the next Section.

#### 2.3. Computational Modeling

To gain a deeper understanding of the surface reaction processes and the most active sites, we performed DFT calculations on a variety of Zn and ZnO structures including pristine close-packed surfaces, stepped surfaces, and rough surfaces with Zn adatoms arranged in different configurations. The structures of the active sites are presented in Figures S11–S21, in Sections S6.1–S6.4, Supporting Information. Full details of the simulations can be found in Section S5, Supporting Information.

We first sought to understand if the amount of oxygen vacancies formed on OD-Zn and ED-Zn, after CO2 electrolysis, could be related to the degree of undercoordination of the two catalysts (Section 2.1). To do so, we determined the free energies and associated potentials for the formation of oxygen vacancies on ZnO surfaces with various degrees of undercoordination (Table S7, Supporting Information). Overall, we found that the free energies for the formation of an oxygen vacancy were more favorable on step edges (0.30 eV) as compared to on terraces (0.80 eV). In other words, oxygen vacancies are more easily formed on rough metal oxides. This finding shows that, by virtue of its roughness, OD-Zn likely has more undercoordinated Zn sites under CO2RR conditions. These sites, consequently, re-oxidized to ZnO with a higher concentration of oxygen vacancies under atmospheric conditions, as shown in the characterization experiments.

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For CO<sub>2</sub> reduction to CO, there are generally two adsorbed intermediates, namely \*COOH and \*CO.<sup>[56,57]</sup> These are formed upon successive proton-electron transfers. In **Figure 4**, we present the trends in adsorption energies of \*COOH and \*CO on Zn surfaces as a function of generalized coordination



**Figure 4.** Adsorption energies of a) \*COOH with respect to  $CO_2(g)$  and a proton/electron pair, and b) \*CO with respect to CO(g) as a function of the generalized coordination number ( $\overline{CN}$ ). MAE stands for mean absolute error and corresponds to the average vertical difference between the DFT-calculated datapoints and the linear fit. For instance, the MAEs of 0.09 and 0.11 eV in (a) and (b) indicate that, on average, the calculated datapoints deviate by 0.09 and 0.11 eV from their linear fits. The gray channels below and above the linear fits correspond to  $\pm 1.5$  MAE. The dashed line in (b) corresponds to an average adsorption energy of 0.51 eV, which leads to a MAE of 0.12 eV. Structures of the active sites are shown in Figures S11–S21, Supporting Information, and the adsorption configurations of \*COOH are shown in Figures S25–S35, Supporting Information.

numbers  $(\overline{CN})$ .<sup>[58]</sup>  $\overline{CN}$  is a first-order extension of conventional coordination numbers that weighs every first-nearest neighbor by its corresponding coordination number. In other words, the second-nearest neighbors are incorporated into the counting. This allows for the distinction of seemingly identical sites and the description of finite-size effects. In addition, strain effects can be accounted for.<sup>[59]</sup>

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The adsorption energies of \*COOH increase as the coordination of the active sites decreases (Figure 4). The binding of \*CO, in contrast, is generally constant and weak on the Zn sites. This implies that its residence time on the surface is likely short, which allows us to model the following simplified pathway for  $CO_2$  reduction to CO:

$$* + CO_2 + H^+ + e^- \rightarrow * COOH \tag{1}$$

$$*COOH + H^+ + e^- \rightarrow * + CO + H_2O$$
<sup>(2)</sup>

The free-energy diagrams based on Equations (1) and (2) for 11 different sites on Zn and ZnO surfaces are summarized in Table S8 and Figure S23, Supporting Information, contains the onset potentials for all these active sites. From these results, we construct a coordination–activity plot, which shows the CO<sub>2</sub>RR overpotentials based on the adsorption energies of Equations (1) and (2) ( $\eta = U_{eq} - \max(\Delta G_1, \Delta G_2)/e^-$ , where  $U_{eq} = -0.105 \text{ V}, \Delta G_1 = \Delta G_{*COOH}$ , and  $\Delta G_2 = \Delta G_{eq} - \Delta G_{*COOH}$ , with  $\Delta G_{eq} = -2U_{eq} = 0.21 \text{ eV}$  being the overall reaction energy) as a function of  $\overline{CN}$  (Figure 5). Since  $\overline{CN}$  can only be defined for metals, the inset in Figure 5 provides a conventional Sabatier-type volcano plot (see further details in Figure S24, Supporting Information) using  $\Delta G_{COOH}$  as the descriptor, allowing



**Figure 5.** Additive inverse of the overpotential  $(-\eta)$  as a function of the generalized coordination number  $(\overline{CN})$ . The overpotential was calculated as  $\eta = U_{eq} - \max(\Delta G_1, \Delta G_2)/e^-$ , as described in the text. The scaling lines were obtained from the trends in the adsorption energies in Figure 4a for both sides of the volcano. The gray channels below and above the scaling lines correspond to  $\pm 1.5$  MAE. Inset: Sabatier-type volcano plot as a function of the adsorption energies of \*COOH (see labeled datapoints in Figure S24, Supporting Information).

us to include both Zn and ZnO surfaces in the same plot (see labeled datapoints in Figure S24, Supporting Information).

Following a previous publication on the topic,<sup>[27]</sup> we calculated the reaction energetics on Zn(0001) and ZnO(0001), and the CO<sub>2</sub>RR onset potentials on these surfaces were predicted to be -0.79 and -1.16 V, respectively (Table S8 and Figures S23 and S24, Supporting Information). We further found that an oxygen vacancy in ZnO(0001) will increase the activity for CO<sub>2</sub>RR, as the onset potential improved from the aforementioned -1.16 to -0.79 V due to the strengthening of the \*COOH binding energy. Although this decrease is substantial, the onset potential is still relatively far from the experimental onset potentials of ED-Zn and OD-Zn (-0.40 V). This suggests that sites with higher activities should be present on our catalysts.

Reducing the coordination of the (0001) facets of Zn and ZnO leads to the regularly stepped Zn(105) and ZnO(105) surfaces, both of which contain two step types: rectangular step edges and triangular step edges (Figures S12 and S18, Supporting Information). The two surfaces showed similar reaction energetics, with onset potentials of -0.23 and -0.26 V, respectively. More undercoordinated surfaces, such as Zn adatom chains, triangles, and pyramids on the Zn(0001) surface (shown in Figures S13–S15, Supporting Information) have onset potentials ranging from -0.20 to -0.36 V, with the lowest onset potential realized on the adatom triangle on the Zn(0001) surface.

For adatom clusters (one adatom, a triangle, and a pyramid, shown in Figures S19-S21, Supporting Information) on a ZnO surface, which illustrate how a partially reduced ZnO surface would catalyze CO<sub>2</sub>RR, we found that an isolated Zn adatom on the ZnO(0001) surface is less favorable (-1.36 V) than any other system we simulated. However, larger adatom clusters (triangles and pyramids) on ZnO share similar onset potentials (-0.27 and -0.36 V) as the Zn adatoms on the metallic Zn surface. We note that the computed onset potentials on undercoordinated surfaces are as low as -0.20 V, which differ from the experimentally determined onset potential of -0.40 V (Section 2.2). This suggests that the different sites (be it oxygen vacancies, stepped surfaces, pristine Zn, adatoms on Zn or ZnO surfaces) could all be present in the catalyst and contribute to CO<sub>2</sub>RR, but to different extents, depending on the corresponding site densities.

Last, in Figure 5, we estimate that sites with  $\overline{CN} \approx 3$  (which corresponds to  $\Delta G_{\text{COOH}} \approx 0.105 \text{ eV}$ ) provide the lowest onset potential for CO<sub>2</sub>RR to CO. Such a coordination number corresponds to highly undercoordinated sites, such as those at Zn clusters over extended surfaces. In addition, other undercoordinated structures such as step edges at Zn(105) also provide favorable overpotentials. Again, the density of the specific sites under reaction conditions determines which ones contribute the most to the overall activity.

All in all, we conclude that surfaces with highly undercoordinated sites provide higher activities, which mirrors our experimental observations. Previous works on Zn have suggested that the presence of oxygen vacancies and high electrochemical surface areas contribute to their high CO<sub>2</sub>RR activities.<sup>[25–28,32,33]</sup> While  $j_{CO}$  does increase with higher electrochemical surface areas, we note that there is a distinct difference in activities when comparing ED-Zn to OD-Zn electrodes with similar roughness factors. This would seemingly suggest

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that oxygen vacancies in OD-Zn could indeed result in more favorable activity. However, our DFT calculations showed that while oxygen vacancies lower the onset potentials for CO production compared to that of pristine Zn(0001) and ZnO(0001), highly undercoordinated surfaces with small Zn clusters exhibited even lower onset potentials, due to their nearly optimal \*COOH adsorption energies. Therefore, instead of attributing the enhancement in CO<sub>2</sub>RR activity to higher amounts of oxygen vacancies is likely to contribute to a larger extent to the enhanced CO<sub>2</sub>RR performance.

## 3. Conclusion

We have presented the in situ transformation of ZnO particles into porous dendrites during CO<sub>2</sub>RR. The oxide-derived Zn (OD-Zn) dendrites are selective, active, and stable for electrocatalyzing CO<sub>2</sub> reduction to CO. The  $j_{CO}$  was found to correlate with the roughness of the electrodes. Using OD-Zn<sub>2.5</sub> as catalyst, CO<sub>2</sub> could be reduced to CO with a maximum FE of 86% at -0.95 V and partial current density of -266 mA cm<sup>-2</sup> at -1.00 V. Electrodeposited Zn (ED-Zn), in contrast, had consistently lower FE<sub>CO</sub> and  $j_{CO}$ . Raman spectroscopy, XPS, and DFT pinpointed a larger concentration of highly undercoordinated Zn sites on OD-Zn, as compared to on ED-Zn.

DFT-based electrocatalysis modeling of a ZnO surface with oxygen vacancies showed only moderate improvements in the onset potential as compared to pristine Zn and ZnO surfaces. This indicates that while oxygen vacancies improve the performance of ZnO terraces, they do not correspond to the most active sites for  $CO_2RR$ . Instead, highly undercoordinated sites exhibited significantly more favorable onset potentials, regardless of the underlying substrate being metallic or partially reduced. The highly defective sites facilitate both the formation of \*COOH and its further hydrogenation to ultimately produce  $CO_{(g)}$ .

All these findings indicate that suitably engineered ZnOderived materials can potentially be an alternative to the more costly CO-producing Ag and Au electrocatalysts, and that the main guideline for their design is to increase the undercoordination of the catalytic sites.

## 4. Experimental Section

Detailed experimental procedures can be found in Section S1, Supporting Information. The DFT calculations were made with VASP,<sup>[60]</sup> and the computational electrocatalysis models used the computational hydrogen electrode;<sup>[61]</sup> semi-empirical gas-phase corrections<sup>[57]</sup> and solvent-adsorbate interactions calculated via micro-solvation<sup>[62]</sup> were both incorporated in the assessment of the free energies. Further details can be found in Sections S5 and S6, Supporting Information.

# **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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# **Conflict of Interest**

The authors declare no conflict of interest.

# **Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## Keywords

carbon monoxide,  $\mbox{CO}_2$  reduction, density functional theory, electrocatalysis, zinc dendrites

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