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# The Interactive Dynamics of Nanocatalyst Structure and Microenvironment during Electrochemical CO<sub>2</sub> Conversion

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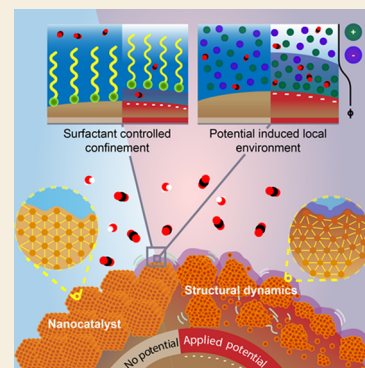
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**ABSTRACT:** In the pursuit of a decarbonized society, electrocatalytic CO<sub>2</sub> conversion has drawn tremendous research interest in recent years as a promising route to recycling CO<sub>2</sub> into more valuable chemicals. To achieve high catalytic activity and selectivity, nanocatalysts of diverse structures and compositions have been designed. However, the dynamic structural transformation of the nanocatalysts taking place under operating conditions makes it difficult to study active site configurations present during the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR). In addition, although recognized as consequential to the catalytic performance, the reaction microenvironment generated near the nanocatalyst surface during CO<sub>2</sub>RR and its impact are still an understudied research area. In this Perspective, we discuss current understandings and difficulties associated with investigating such dynamic aspects of both the surface reaction site and its surrounding reaction environment as a whole. We further highlight the interactive influence of the structural transformation and the microenvironment on the catalytic performance of nanocatalysts. We also present future research directions to control the structural evolution of nanocatalysts and tailor their reaction microenvironment to achieve an ideal catalyst for improved electrochemical CO<sub>2</sub>RR.



**KEYWORDS:** Electrochemical CO<sub>2</sub> reduction, Nanocatalysts, Structural transformation, Catalytic microenvironment, Heterogeneous electrocatalysis

## 1. INTRODUCTION

The anthropogenic CO<sub>2</sub> emissions into the atmosphere have undoubtedly accelerated climate change over the past several decades.<sup>1</sup> Hence, there is an immediate need for technological advances to capture and recycle CO<sub>2</sub>, in order to approach a more sustainable circular carbon economy. In this regard, electrochemical CO<sub>2</sub> conversion, potentially powered with increasingly available renewable energy sources, is one of the promising technologies that can upgrade CO<sub>2</sub> into value-added fuels and chemicals (e.g., CO, C<sub>2</sub>H<sub>4</sub>).<sup>2</sup> As part of this technology, catalysts that perform the electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) at the cathode have been a key focus of recent research endeavors as they govern the product yield rate and selectivity, largely determining the overall energy efficiency of the process.<sup>3</sup>

In particular, the well-defined compositions and structures of nanocatalysts have made them excellent platforms to gain insights into the catalyst structure–performance relationship.<sup>4,5</sup> The well-controlled synthesis of nanocatalysts allows for the direct application of experimental and theoretical understandings to the rational design of an electrocatalyst with enhanced catalytic activity (i.e., turnover) and desired product selectivity.<sup>6,7</sup> Therefore, understanding the correlation between the structural features of as-synthesized nanocatalysts and their

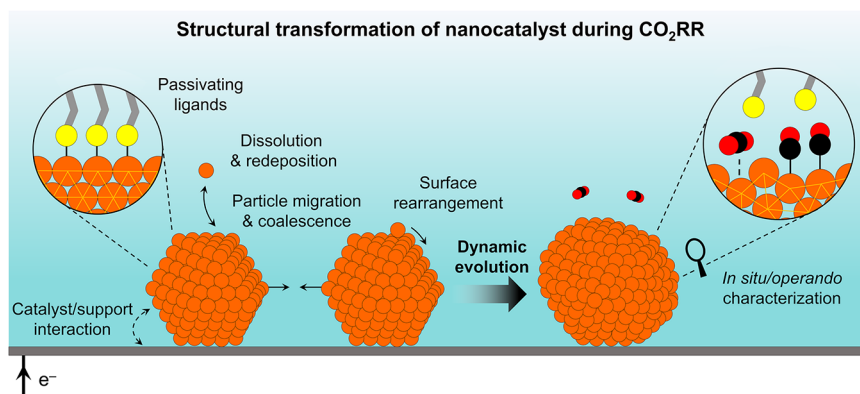
catalytic performance have been the preferred approach in catalyst development.

However, once exposed to operating conditions, nanocatalysts are prone to structural transformation as a result of the surface polarization and their interactions with reaction species (e.g., reactant and intermediate), conducting support (e.g., graphitic carbon paper), organic ligands used in their synthesis, and surrounding electrochemical environment (e.g., electrolyte species). Additionally, with a given energy input, the higher surface energy of nanocatalysts that stems from a larger surface area to volume ratio in comparison to bulk equivalents favors their mobility. This overall high surface energy leads to the observation of more drastic surface atom migration and possible nanocatalyst coalescence under applied bias. Although acknowledged, the implications of the dynamic aspect of such structural evolution on the catalytic performance of CO<sub>2</sub> electrolysis remain elusive and warrant more studies.

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**Figure 1.** Schematic illustration of structural transformation of nanocatalyst occurring under  $\text{CO}_2$ -reducing condition. During the dynamic structural evolution of nanocatalysts, dissolution and redeposition of nanocatalyst atoms, particle migration and coalescence, and atomic surface rearrangement are likely to occur simultaneously. This process leads to the transition of nanocrystals from a well-defined structure to a more dynamic structure. *In situ/operando* characterization is essential to better understand catalytic active sites during  $\text{CO}_2$ RR. Orange, black, and red spheres represent catalyst atom, carbon, and oxygen, respectively. Yellow sphere with a gray chain indicates a nanocrystal-capping ligand.

Besides the structural dynamics taking place at their surface, nanocatalysts' catalytic activity induces reciprocal changes on their surroundings (e.g., reactant/intermediate species concentration, local pH, etc.), thus contributing to the formation of a regime with unique physicochemical properties that differ from the bulk. This confined regime, often referred to as the microenvironment in catalysis, plays an important role in mediating the parameters, directly affecting the reaction at the nanocatalyst surface. Considering its definitive influence on the catalytic performance for  $\text{CO}_2$ RR, the microenvironment formed near the nanocatalyst surface also calls for further studies. Such insights will become critical to ultimately optimize the reaction environment necessary for enhanced catalytic performance.

In this Perspective, we discuss the collaborative impact of nanocatalysts' structure and microenvironment dynamics on the electrocatalytic  $\text{CO}_2$  conversion. Overall, we underscore the importance of understanding and controlling the dynamic aspects of nanocatalysts from a holistic point of view in order to achieve improved  $\text{CO}_2$  electrolysis. From this insight, we suggest future research directions needed to expand the range of catalytic performance in the field of  $\text{CO}_2$  electroconversion.

## 2. STRUCTURAL TRANSFORMATION OF NANOCATALYST DURING $\text{CO}_2$ RR

The structural rearrangement of catalysts under operating conditions has been commonly observed for various types of heterogeneous catalysis and across different scales (e.g., macroscopic, nanoscopic). In particular, an electrocatalyst surface during  $\text{CO}_2$  conversion interfaces with a variety of electrolytic species as dictated by the applied bias. Also, the thermodynamically stable phase of the catalysts in aqueous media is determined by electrode potential, pH, and ionic concentration according to the Nernst equation (i.e., Pourbaix diagram). In addition, strong binding of intermediate species produced during  $\text{CO}_2$ RR on a catalyst surface (e.g., adsorbed CO) can weaken the metal–metal bonds at the surface and readily induce migration of surface atoms.<sup>8,9</sup> Metal electromigration has also been recently proposed as another mechanism for the phenomenon of structural reconstruction.<sup>8</sup>

In light of these dynamic reconstructions occurring during electrocatalytic reactions, the nanocatalyst design concepts employed for  $\text{CO}_2$  electrocatalyst have greatly evolved in

recent years. Progressively, the synthetic efforts traditionally focusing on a well-defined structure isolated from the reaction environment have moved to a more comprehensive evaluation of the changing nature of electrocatalysts.<sup>10–12</sup> The insights gained from structurally evolving catalysts have become essential to understanding active site configurations and optimizing the resulting catalytic performance. Several examples have demonstrated that the *ex situ* structures characterized before and after  $\text{CO}_2$  electrolysis, while relevant to some degree, are not sufficient to predict the properties of the active state formed during the reaction.

Below, we will address the current understanding of the structural transformation of nanocatalysts during  $\text{CO}_2$  electrocatalysis with an emphasis on its dynamic aspect and recent efforts to investigate such phenomena. We also discuss how to exploit the potential benefits of catalyst structural transformation as a way to optimize the electrochemical  $\text{CO}_2$  conversion. Although there has been parallel effort in isolating which features are fundamentally beneficial to improve  $\text{CO}_2$  electroreduction using more stable and better defined surfaces (e.g., single crystal),<sup>13,14</sup> we offer here an alternative insight in the diversity of active sites attainable through the remarkable structural transformation of nanomaterials. Together with theoretical studies, we highlight how such an approach can further deepen our understanding about the potential of exploiting nanocatalysts as better suited yet tunable  $\text{CO}_2$  reducing catalysts.

### 2.1. Potential Induced Transformation

The application of electrochemical bias relevant for  $\text{CO}_2$ RR provides an energy input that accompanies drastic structural reconstruction (Figure 1).<sup>15</sup> As also seen in thermal catalysis, rearrangement mechanisms such as surface atom migration and particle coalescence are observed during  $\text{CO}_2$  electrolysis. In particular, Cu catalysts display more complex structural transformations during  $\text{CO}_2$ RR due to copper's stronger interaction with intermediate species (e.g., stronger binding of CO intermediate), besides their greater susceptibility to oxidation, in comparison with noble metal-based catalysts. In order to study such dynamic events happening under operating conditions, *in situ* or *operando* techniques have been preferred including surface spectroscopy and microscopy techniques. For instance, Gunathunge et al. provided spectroscopic evidence for reversible potential-induced structural transformation of

polycrystalline Cu surfaces. Concretely, adsorbed CO intermediates were observed on newly formed undercoordinated sites via *in situ* infrared and Raman spectroscopy.<sup>16</sup> Recently, Phan et al. used electrochemical atomic force microscopy (EC-AFM) to more directly probe the dynamic morphological changes of the single-crystalline Cu(100) surface occurring under CO<sub>2</sub> reducing conditions.<sup>17</sup> These *in situ* studies showcase that far from static, the catalyst morphology during CO<sub>2</sub>RR is rather dynamic.

While these works focus on the structural rearrangement of macroscopic Cu catalysts following the application of bias, such behavior has also been studied for nanocatalysts which tend to exhibit more drastic structural changes.<sup>18</sup> Buonsanti and co-workers have shown the loss of sharp edges in Cu nanocubes across different sizes and the appearance of nanoclusters during CO<sub>2</sub> electrolysis.<sup>19</sup> It was claimed that negative potential applied for CO<sub>2</sub>RR causes such nanoclustering as a dominant degradation mechanism. In another work from the same group, *in situ* transmission electron microscopy (TEM) in conjunction with *operando* X-ray absorption spectroscopy (XAS) was utilized to study the structural transformation of Cu nanoparticles under CO<sub>2</sub>RR relevant conditions.<sup>20</sup> Their measurements suggested the dissolution and redeposition of Cu nanocatalysts as a structural transformation pathway.

Furthermore, several studies have shown more dramatic structural transformation of Cu nanocatalysts through nanoparticle coalescence during CO<sub>2</sub> electrolysis. For example, Kim et al. reported the structural evolution of a monodisperse Cu nanoparticle ensemble from a close-packed monolayer to the formation of cube-like nanocrystals observed *ex situ* post-electrolysis.<sup>21</sup> Later, it was further found via *in situ* TEM and XAS that such a drastic structural change resulted from the strikingly rapid nanoparticle coalescence occurring under CO<sub>2</sub>-reducing bias, followed by their instant oxidation after electrolysis.<sup>22</sup> Importantly, it was demonstrated that a catalytically active nanostructure can be made as a result of the dynamic structural evolution, contrary to the conventional notion that nanocatalyst coalescence is detrimental to CO<sub>2</sub> electroconversion activity.

Although these potential-induced structural transformations have not been fully understood, the variety of structural evolution mechanisms accessible in CO<sub>2</sub> electrocatalysis ensures that a broader range of active structures can be achieved especially for nanocatalysts. Furthermore, more complex structural evolution can take place as a result of the addition of an additional element (see Section 3.2. for more detailed discussion on bimetallic systems). In other words, there exist abundant research opportunities to utilize the structural evolution of catalysts in a controllable way to create new nanocatalysts with enhanced activity and selectivity for CO<sub>2</sub> electrocatalysis. Additionally, insights obtained from *in situ* characterization techniques will become inherent to assessing the catalytic benefits of such structural evolution.

## 2.2. Driving CO<sub>2</sub>RR on Dynamic Surfaces

The structural transformation of nanocatalysts during CO<sub>2</sub>RR has generally been associated with the deactivation of desired active sites while favoring other unintended reaction pathways or an unwanted competing reaction, such as the hydrogen evolution reaction (HER). However, some examples have demonstrated that in turn, the structural rearrangement of nanocatalysts can lead to the formation of reaction sites with

higher intrinsic activity toward CO<sub>2</sub>RR.<sup>22,23</sup> Therefore, it is critical to identify which structural features generated under CO<sub>2</sub>-reducing conditions can benefit the catalytic performance of nanocatalysts.

Traditionally, the exposed facets of Cu-based nanocatalysts have been identified as a selectivity descriptor. For both macroscopic and nanoscopic Cu surfaces, Cu(100) and Cu(111) facets have been correlated with higher C<sub>2</sub>H<sub>4</sub> or CH<sub>4</sub> turnover, respectively.<sup>24,25</sup> The proportion of edges and corners has also been identified as a key feature in tuning the CO<sub>2</sub>RR selectivity.<sup>26</sup> However, the formation and stabilization of such crystalline features is incredibly challenging on structurally evolving electrocatalysts. Additionally, although characterization methods have been employed to monitor the structural transformation of Cu electrocatalysts under operating conditions (e.g., EC-STM),<sup>14</sup> these studies often remain limited to macroscopic well-defined crystalline surfaces and are rarely reported for nanocatalysts. Guiding the design of structurally evolving nanocatalysts using theoretical insights is therefore demanding and often limiting. For example, the work of Choi et al. showed that the structural features formed during CO<sub>2</sub> electrolysis on a Cu(100) nanowire further enhanced its C<sub>2+</sub> selectivity over C<sub>1</sub>.<sup>27</sup> This catalytic improvement was associated with the increase in the density of steps on the nanowire surface (i.e., a combination of Cu(100) and Cu(111) facets). Therefore, although heterogeneous, the formation of active sites that occurs during electrocatalysis on structurally evolving nanocatalysts can reach superior performance over that predicted by theory.

Although potentially beneficial, there remains a lack of consensus in the literature regarding whether the structural transformation taking place during electrolysis is responsible for catalytic degradation or improvement. For example, Huang et al. identified the nanoclustering taking place on Cu nanocrystals as a degradation process that reduces the catalytic activity over time, correlating low coordination sites with a rise in the HER at the expense of CO<sub>2</sub>RR.<sup>19</sup> Along this line, a similar claim was supported computationally in the work by Wang and co-workers, highlighting that lower-coordinated sites promote both \*H and \*CO binding.<sup>28</sup> Meanwhile, other theoretical studies demonstrated that coordinately unsaturated sites facilitate the C–C coupling step essential to multicarbon (C<sub>2+</sub>) formation as a result of higher CO coverage enabled by stronger \*CO binding sites.<sup>29</sup> The disparity in the catalytic benefits inferred by an increase of undercoordinated sites during CO<sub>2</sub>RR makes it difficult for the community to identify which key features to favor for the design of CO<sub>2</sub>RR electrocatalysts.

Nonetheless, in spite of their potential disadvantage, there is a sizable number of works that have consistently corroborated the increase in the CO<sub>2</sub>RR activity and the C<sub>2+</sub> selectivity upon increasing the undercoordination formation of Cu nanocatalysts.<sup>22,27,30,31</sup> Thus, this suggests the necessity to further explore this hypothesis toward enhanced CO<sub>2</sub>RR catalytic performance. As part of this effort, one representative study is the work by Li et al. where the dramatic structural evolution of a Cu nanoparticle ensemble during CO<sub>2</sub>RR, termed *electrochemical scrambling*, leads to a distinct enhancement in C<sub>2+</sub> selectivity and activity.<sup>22</sup> This enhancement was associated with the formation of undercoordinated Cu sites characterized by extended X-ray absorption fine structure (EXAFS) analysis. This work strongly supports the correlation between undercoordinated site formation and the intrinsically higher activity

(i.e., specific activity) of this Cu NP ensemble toward  $C_{2+}$  formation. Additionally, the formation of such sites was found to take place rapidly at the beginning of electrolysis and achieve a metastable state capable of sustaining stable catalytic activity. The reconstruction event leading to undercoordinated site formation was therefore identified as a new catalytic active site formation process, rather than degradation process.

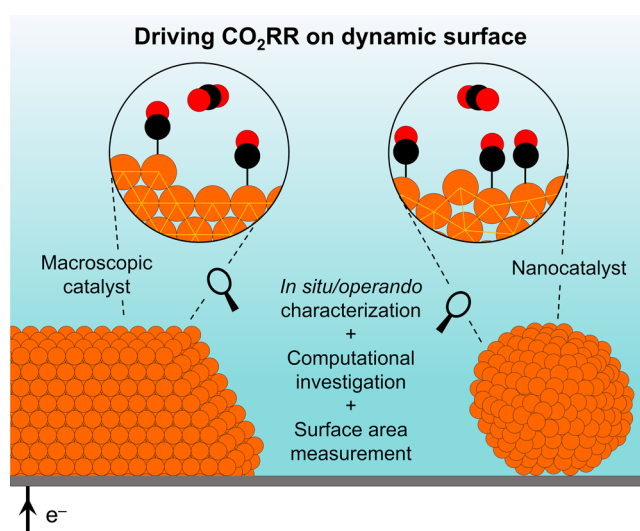
To adequately assess the benefits of a surface formed as a result of structural reconstruction (e.g., undercoordinated sites), systematic experimental and theoretical approaches are preferable. Well-defined macroscopic and nanoscopic catalyst surfaces with different orientations and coordination numbers (e.g., single crystals, well-defined nanocatalysts, atomically precise clusters) are better suited starting materials to track a structural evolution triggered under  $CO_2$ -reducing conditions. Investigating such a dynamic process will be greatly improved by using *in situ/operando* techniques and carrying out parallel theoretical studies that will provide complementary molecular-level insights into active sites and associated mechanistic reaction pathways for  $CO_2RR$ .

In addition, it is of great importance to study the intrinsic catalytic property of active sites and their catalytic function. For instance, in an effort to gauge the chemical interaction between adsorbates and active sites, hydroxyl and sulfate adsorption/desorption have been utilized as a measure of intermediate binding strength on Ag nanocatalysts for  $CO_2RR$ .<sup>32</sup> In another work from our group, underpotentially deposited Pb adatoms were also used as a surrogate for adsorbed intermediate species to study adsorbate binding strength of the evolved Cu catalyst with abundant undercoordinated sites.<sup>22</sup> It was suggested that the undercoordinated sites offer much stronger binding sites for intermediate species for C–C coupling, as can be anticipated from the bond order conservation principle. In this study, the electrochemically active surface area (ECSA) of the catalysts was also measured using Pb underpotential deposition (UPD) to compare the specific  $C_{2+}$  activity, providing more insights into the enhanced C–C dimerization activity compared to conventional polycrystalline Cu catalysts. This normalization is crucial to accurately extract the intrinsic properties responsible for the observation of catalytic enhancement,<sup>33</sup> further supporting the significance of low-coordinated Cu sites as catalytically favorable to  $CO_2$ -to- $C_{2+}$  conversion. Often, by relying principally on *ex situ* characterization further supported by DFT calculations, an improvement in the catalytic activity of a nanocatalyst is too easily associated with a specific structural feature (i.e., facets, steps, kinks). However, such features may result from the process of surface roughening that simultaneously increase the ECSA.

Altogether, to properly evaluate catalytic benefits of active structures newly formed during  $CO_2RR$ , needed are (1) the rigorous characterization of the catalyst features created from the dynamic structural transformation, preferably using *in situ* methods whenever applicable, (2) isolating the inherent catalytic property of such features based on experimental results and theoretical calculations, and (3) the activity normalization using adequate ECSA measuring methods (Figure 2).

### 2.3. Guiding the Dynamics of Nanocatalysts

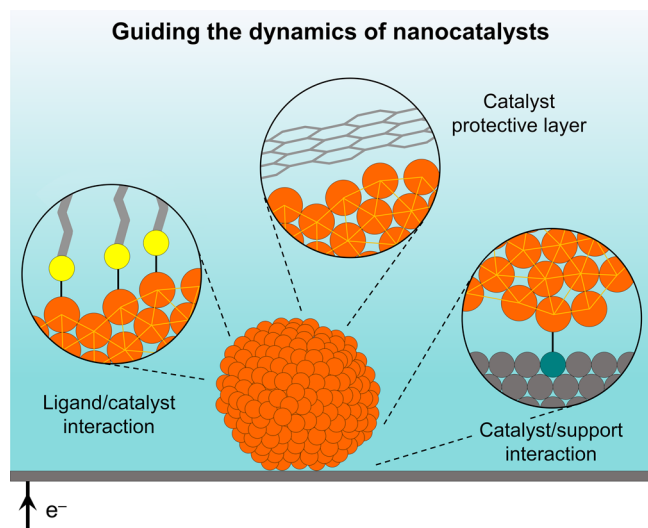
With well-founded understandings, the structural transformation of nanocatalysts can be controlled and exploited to expand the reach of nanocatalyst design that may not be attainable



**Figure 2.** Schematic illustration of dynamic surfaces of catalysts under  $CO_2$ -reducing condition. To gain a molecular-level understanding on electrocatalytic  $CO_2$  conversion occurring on the surface of the dynamic catalyst surface, which tends to be more challenging for nanocatalysts, *in situ/operando* characterization of electrocatalysts combined with theoretical computations is pivotal. Intrinsic catalytic activity of the catalysts (e.g., current toward a  $CO_2RR$  product divided by electrochemically active surface area) should be assessed to correlate the catalytic performance and the structural properties of the catalysts present during  $CO_2$  electrolysis.

through conventional nanomaterial synthesis. However, achieving such transformation toward intrinsically active surfaces in a controlled manner requires guiding principles. Multiple parameters need to be considered including (1) the surface energy of the nanocatalyst that determines its propensity for structural rearrangement prior to the reaction, (2) the surrounding environment it is subject to during  $CO_2$  electrocatalysis, and (3) the nanocatalyst–support interactions. These parameters are convoluted and thus require comprehensive consideration from which various strategies can be devised to guide the evolution of nanocatalysts (Figure 3).

The surface energy is highly dependent on the composition and exposed facets of the nanocatalyst, as well as the molecular species that interact with its surface. This generally involves reaction species adsorbed to surface atoms (i.e., reaction intermediates such as  $*CO$ ), species in the electrolyte (e.g., electrolyte ions, hydroxide ions), and at times, the organic passivating agents used in the synthesis of the nanocatalyst.<sup>9,34</sup> The presence of ligands is an excellent example of how to control the surface properties of a nanocatalyst while mediating interactions with other species. Several works have shown how the presence or absence thereof significantly influence the structural transformation of nanocatalysts during  $CO_2$  electrolysis. In general, the ligand–metal surface binding strength, which is determined by the ligand headgroup and nanocatalyst exposed facets, dictates the resilience of the surface structure to the structural transformation.<sup>35</sup> For instance, with strongly bound ligands, the structural transformation under bias can be deterred, and thus, the nanocatalysts tend to retain their initial structure and catalytic performance.<sup>35,36</sup> Another strategy to preserve the initial morphology of nanocatalysts is to employ a conductive protective layer such as graphene oxide.<sup>37</sup> Wrapping Cu nanowire catalysts with graphene oxide was demonstrated to



**Figure 3.** Schematic illustration of various approaches to guiding the structural evolution of nanocatalysts under  $\text{CO}_2$ -reducing condition. To control and ultimately harness the dynamic transformation of nanocatalysts for enhanced catalytic performance, various strategies can be devised, utilizing ligand/catalyst interaction, catalyst/support interaction, and a catalyst protecting layer.

improve the structural stability while maintaining the electrocatalyst activity.<sup>37</sup>

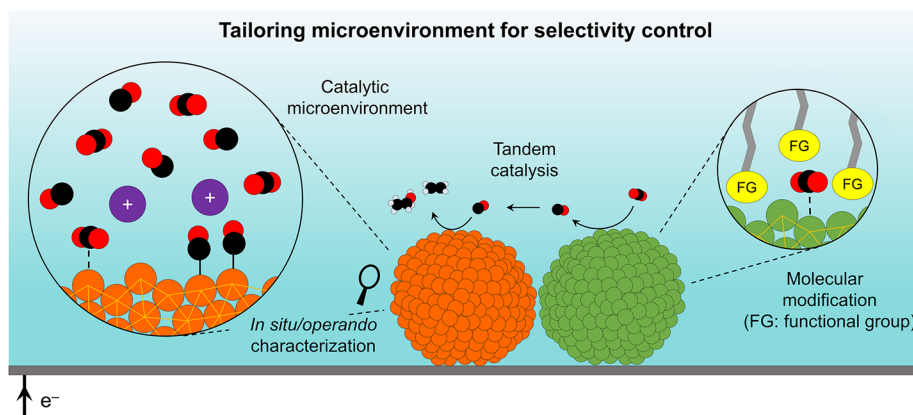
However, these approaches may hamper the access of  $\text{CO}_2$  molecules to active sites and also the formation of potentially more active reaction sites due to a restricted structural transformation. Recently, Chen et al. reported a systematic study of how the removal of surface ligands from Au nanoclusters influences the overall activity of  $\text{CO}_2$ -to- $\text{CO}$  electroconversion.<sup>38</sup> In this work, different thermal and electrochemical treatments prior to  $\text{CO}_2$  electrolysis were conducted to compare their effectiveness in removing the organic ligands, exposing the undercoordinated Au cluster reaction sites, and enhancing catalytic activity. It was also found that harsh treatment conditions can result in excessive nanocluster coalescence and thus a reduction in surface area and the number of undercoordinated sites. Furthermore, an S-doped graphene support used in this work allowed for the

stabilization of the nanoclusters during  $\text{CO}_2\text{RR}$  by anchoring the catalysts through the sulfur–Au cluster interactions. This work highlights the duality between preserving a surface and degrading the accessibility to greater catalytic activity, but it also exemplifies how the nanocatalyst–support interactions can be used as another knob to control the structural transformation during  $\text{CO}_2$  electrolysis.

Therefore, we identify as a primary goal the creation of more active and selective nanocatalysts that may exist in a metastable state as a result of the dynamic structural evolution under  $\text{CO}_2$ -reducing conditions. In this approach, the as-synthesized nanocatalyst can be thought of as a precursor to make a better performing catalyst. One example of this concept is our group's in-depth study on the electrochemical evolution of Cu nanoparticles to undercoordination-rich Cu nanocatalysts, which exhibited a remarkable enhancement in intrinsic activity.<sup>21,22</sup> This approach has attracted growing attention in the  $\text{CO}_2\text{RR}$  research field. For instance, the Sinton group recently demonstrated that low-coordination Cu clusters can be created from controlled *in situ* reduction of molecular catalysts (i.e., Cu(II) phthalocyanine) via carbon nanoparticle confined agglomeration. By driving low-coordination formation, the authors achieved a catalytic selectivity enhancement otherwise unattainable from the original catalyst.<sup>39</sup> We envision that this type of strategy that generates nanocatalysts with improved catalytic performance via structural evolution during  $\text{CO}_2$  electrolysis will open up new avenues for catalyst innovations.

### 3. TAILORING MICROENVIRONMENT FOR SELECTIVITY CONTROL

The performance of a heterogeneous catalyst is often directly associated with its inherent surface properties. However, the environment that surrounds the catalyst also plays a determining role in the catalytic performance, especially in electrocatalysis which requires the presence of electrolyte. Upon application of bias, the effective potential decays away from the surface, thus inducing the formation of an environment with ionic properties distinct from the bulk. Such a difference directly affects the concentration and stabilization of the reactants and other intermediate species involved in the reaction. Therefore, this regime requires careful



**Figure 4.** Schematic illustration of catalytic microenvironment of nanocatalysts during  $\text{CO}_2$  electrolysis and approaches to tuning microenvironment. Dynamic and complex nature of catalytic microenvironment during  $\text{CO}_2\text{RR}$  is depicted in the schematic diagram. Tandem electrocatalysis and molecular modification approaches are promising ways to tailor the microenvironment for improved catalytic performance. Nanocatalysts with different colors indicate dissimilar catalytic selectivity for  $\text{CO}_2\text{RR}$ . FG indicates functional groups in molecular modifiers.

considerations for CO<sub>2</sub>RR, as it entails a broad range of possible reaction pathways, involving multiple electron/proton transfers and intermediate species.

The parameters that define the characteristics of the regime local to the surface are especially complex when considering the electroreduction of CO<sub>2</sub> in aqueous conditions. CO<sub>2</sub> availability largely depends on its interaction with water molecules, which is governed by several equilibria.<sup>40</sup> The chemical nature is also sensitive to the diffusion of CO<sub>2</sub> in the electrolyte as well as the local pH during CO<sub>2</sub>RR. Furthermore, water is a polar solvent that can stabilize polar transition states and intermediates via hydrogen bonding, while participating in the CO<sub>2</sub>RR as a proton donor.<sup>41</sup> Additionally, experimental and theoretical evidence suggest the significance of cation species in mediating the adsorption and stabilization of CO<sub>2</sub> and intermediates through electrostatic interactions, facilitating its reduction.<sup>42–46</sup>

Therefore, optimizing the catalytic performance of CO<sub>2</sub> electroreduction cannot be attained without the comprehensive consideration of all components specific to the environment locally confined to the catalyst surface (i.e., microenvironment) (Figure 4). A better understanding of the synergistic interplay between the catalyst surface and its surroundings and the resulting impact on the progress of the reaction are necessary before eventually tailoring nanocatalysts' microenvironment and tuning their activity toward a more targeted and effective CO<sub>2</sub> electroconversion.

### 3.1. Microenvironment Confined Species Participating in CO<sub>2</sub>RR

CO<sub>2</sub>RR involves multiple electron and proton transfers which depending on the catalyst can lead to a variety of potential intermediates and thus products. To achieve the selective CO<sub>2</sub> electroconversion to a targeted product, it is crucial to favor the formation and stabilization of key intermediates identified so far. However, intermediates are influenced not only by the catalyst surface sites but also by the coexisting surrounding species confined near the catalyst surface (e.g., electrolyte species, surface ligands). Therefore, the molecular population present at the catalyst surface and coexisting with key intermediates should be taken into consideration when investigating the progress of the multistep CO<sub>2</sub> electroreduction reaction.

To probe the molecular landscape formed during CO<sub>2</sub>RR on the catalyst surface and in its close proximity, various surface-sensitive spectroscopic techniques such as *in situ* IR and Raman have been utilized.<sup>47–49</sup> However, a main hurdle remains the detection of intermediate species that may exist at a low concentration in the dynamic electrochemical environment, which may be further exacerbated if these intermediates only reside transiently at the catalyst surface.

Furthermore, it is far more challenging to examine intermediate species that are not bound to the catalyst surface during CO<sub>2</sub>RR. For instance, it has been shown that the stabilization and availability of key intermediates such as CO are essential to the activity and selectivity of CO<sub>2</sub> electroreduction. Multiple works have demonstrated how the high \*CO coverage is necessary to the formation of C<sub>2+</sub> products.<sup>29,50,51</sup> However, although previously suggested to be relevant, the impact of the availability of CO in a regime confined near the surface has not been clearly addressed.

Most recently, a new report has suggested that the formation and retention of CO as an intermediate during CO<sub>2</sub>

electroreduction plays a more critical role than previously anticipated.<sup>52</sup> Specifically, this work suggests the formation of a CO concentrated reservoir that expands beyond the traditional \*CO monolayer coverage. In addition, a clear correlation was established between the density of these intermediates and the rate of C–C coupling leading to the formation of C<sub>2+</sub> products. Along with other works<sup>53,54</sup> that have suggested the presence of near-surface-confined CO intermediates based on spectroscopic observation, this report emphasizes the importance of a microenvironment formed and maintained during CO<sub>2</sub> electrolysis. The significance of an intermediary CO reservoir to promote C–C coupling also entails the necessity to optimize both the C–C coupling ability of the catalyst surface and the local environment to favor the concentration of CO molecules as intermediates. Therefore, new approaches and further advances in spectroscopic techniques that will enable us to investigate intermediates at and near the catalyst/electrolyte interface are needed to better define the catalytic impact of the microenvironment.

### 3.2. Tandem Electrocatalysis Approach

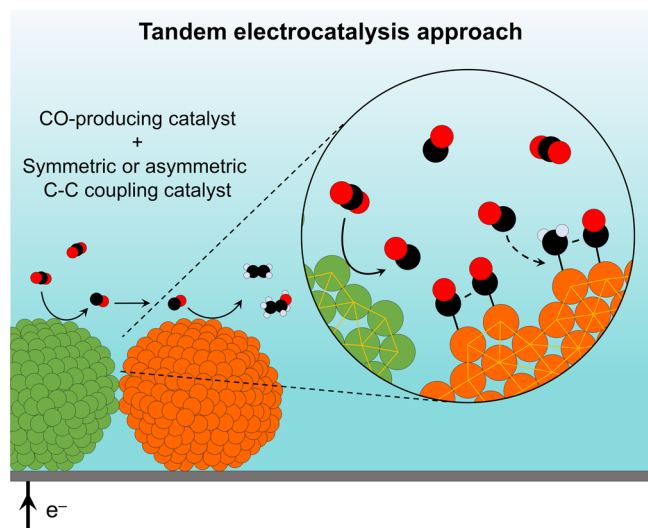
Tandem catalysis is a promising strategy to tailor the catalytic microenvironment, where two or more distinct catalytic sites are closely located to achieve sequential reactions, which in turn can enhance catalytic activity and better tune product selectivity.<sup>55</sup> To this end, nanocatalysts have been designed using multiple elements that can individually carry out different reaction steps, improving the overall efficiency of complex multistep reactions. The combination of reaction sites that (1) improve the availability of key intermediates together with different reaction sites that (2) convert these intermediates to a final product is fundamental to the tandem catalysis approach.

When applied to the electroconversion of CO<sub>2</sub> to multi-carbon products, the tandem approach is especially powerful, as this reaction involves a complex reaction tree leading to a variety of products. Hence, identifying important intermediate species at the branching points of a reaction pathway and understanding the rate-determining steps are crucial when guiding the reaction outcome of CO<sub>2</sub> electrocatalysis through the tandem approach.

One prominent approach for tandem CO<sub>2</sub> electrolysis is the pairing of CO-selective catalysts such as Ag and Au catalysts, together with Cu catalysts capable of efficient C–C coupling (Figure 5). Surface adsorbed CO is widely recognized as a key intermediate for C<sub>2+</sub> formation. Therefore, the CO spillover effect with relatively short surface diffusion or a high CO concentration obtained from nearby CO-generating sites can provide a microenvironment that promotes C–C coupling.<sup>56,57</sup>

Our research group explored this tandem strategy by codepositing Ag and Cu nanoparticles on a gas-diffusion electrode for high-rate, tandem CO<sub>2</sub> electrolysis.<sup>58</sup> In comparison to the Cu nanoparticle system in CO<sub>2</sub>- or CO-reducing conditions, the combination of two distinct active sites significantly improved the turnover of C<sub>2+</sub> products including ethylene and ethanol. In addition, no structural or electronic interactions were observed between Cu and Ag nanocatalysts post-electrolysis. These results suggest that such catalytic improvement solely results from the CO-enriched microenvironment generated by Ag active sites and made available to the nearby Cu active sites.

However, it is worth noting that for Cu-based tandem CO<sub>2</sub> electrolysis, the thermodynamic miscibility of the other elements used in concert with Cu is an important factor to



**Figure 5.** Schematic illustration of tandem electrocatalysis approach for  $\text{CO}_2\text{RR}$ . Nanocatalysts with dissimilar catalytic selectivity are placed close to each other to achieve tandem  $\text{CO}_2\text{RR}$ . Green nanocatalyst represent a CO-producing catalyst, while orange nanocatalyst represent a symmetric (e.g., CO dimerization) or asymmetric (e.g.,  $\text{CO}-\text{CH}_x$  coupling) C–C coupling catalyst.

consider.<sup>59</sup> For instance, Au can form alloys and intermetallic compounds with Cu. Thus, although the Au and Cu phases in a nanocatalyst are initially spatially separated, they tend to form alloys through structural reconstruction during  $\text{CO}_2\text{RR}$ , removing two distinct catalytic domains.<sup>56</sup> Moreover, despite a large miscibility gap in their phase diagram, bimetallic nanocatalyst systems, for example, containing Cu and Ag, may potentially also form surface alloys as a result of structural rearrangement under  $\text{CO}_2$ -reducing conditions. The dynamic element of the nanocatalyst introduces another way to tune the binding properties of a bimetallic catalyst as a whole that differ from those of its individual metallic site. Thus, thorough post-electrolysis *ex situ* material characterization is necessary and should be done *in situ* whenever possible to understand the origin of the measured catalytic performance and verify the presence of a tandem system.

Furthermore, for tandem  $\text{CO}_2$  electrocatalysis to be successful, the energetic feasibility of coupling intermediate species should be carefully considered. Besides the prevailing research interest in the CO spillover and subsequent CO dimerization, recent reports have also suggested the coupling of  $^*\text{CO}$  and  $^*\text{CH}_x$  through the combination of nanocatalysts with dissimilar  $\text{CO}_2\text{RR}$  selectivity.<sup>60–62</sup> For example, Ting et al. used  $\text{Cu}_2\text{O}$  nanowires ( $\text{CH}_x$ -forming catalyst) decorated with Ag nanoparticles (CO-forming catalysts), creating a bimetallic catalyst system, which exhibited 5-fold higher catalytic activity toward ethanol than pure  $\text{Cu}_2\text{O}$  nanowires.<sup>60</sup> Using computational modeling, they suggested the coupling between  $^*\text{CO}$  and  $^*\text{CH}_x$  to be energetically more favorable than  $^*\text{CO}$  dimerization and a main reaction pathway toward ethanol production. Their calculations also indicated that the coupling of these intermediates likely occurred at the Cu–Ag boundaries via a Langmuir–Hinshelwood-type mechanism rather than the previously suggested CO insertion pathway (Eley–Rideal mechanism).<sup>60,63,64</sup>

Although promising, the tandem approach still faces some challenges. First, the applied potentials necessary to achieve the target microenvironment composition and to optimize its

utilization to a final product are not necessarily coincidental. For instance, CO can be produced at high rates with relatively low overpotentials by Ag nanocatalysts; however, Cu nanocatalysts may not be able to consume CO effectively for further reduction at the same applied potentials.<sup>57</sup> Additionally, a similar difficulty emerges when attempting to coproduce different intermediate species (e.g., CO and  $\text{CH}_x$  from Ag and Cu, respectively) at comparable current densities prior to their subsequent coupling. To address these challenges, approaches including the optimization of the spatial proximity and relative density of different active sites should be considered. Also, alternating the applied potential through pulsing can be a useful approach to align the production rates of different intermediate species such as CO and  $\text{CH}_x$  from Ag and Cu bimetallic systems. At a low bias, Ag-based catalysts can efficiently generate CO, while Cu-based catalysts would remain relatively inactive. On the other hand, at a high bias, Ag-based catalysts can achieve an increased production rate of CO; meanwhile, Cu-based catalysts start producing  $\text{CH}_x$  and utilizing the CO from Ag-based catalysts for tandem asymmetric coupling.

Eventually, establishing a better understanding of how the microenvironment created during  $\text{CO}_2\text{RR}$  in tandem catalytic systems can benefit the selectivity will greatly rely on *in situ* or *operando* spectroscopic techniques. The resulting information on which intermediates in what environment lead to the formation of a specific product will allow modulation of the design of future tandem platforms in accordance with the targeted product. Simultaneously, the use of *in situ* characterization methods should be utilized whenever possible to ensure that despite potential structural evolution, the tandem character of the employed catalyst is preserved during the  $\text{CO}_2\text{RR}$ .

### 3.3. Molecular Modification Approach

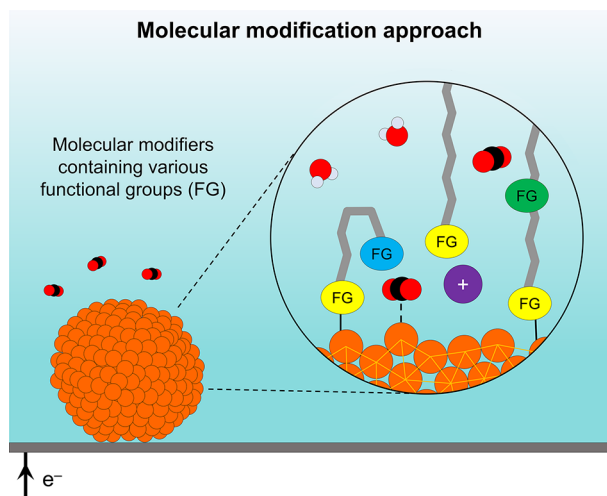
Conventionally, although necessary for the colloidal synthesis of nanocatalysts, organic ligands have sometimes been considered a detrimental component for the purpose of catalysis as they can block reaction sites. Thus, in many cases, they are deliberately removed before their use in electrocatalytic reactions by various methods, such as thermal annealing, plasma treatment, or electrochemical stripping.<sup>65</sup>

However, in an effort to overcome scaling relations associated with metal surface atoms of nanocatalysts, surface ligands have recently received significant research interest as a new way to tune nanocatalyst selectivity for  $\text{CO}_2\text{RR}$ .<sup>66,67</sup> The interactions of organic surface ligands with nanoparticle metal sites and  $\text{CO}_2$  molecules/intermediate species can modulate the properties and thus the effects of the microenvironment on the reaction progress during  $\text{CO}_2$  electrolysis (Figure 6).

First, tethered surface ligands can interact with the nanocatalyst surface as a molecular modifier that changes the electronic structure of the surface metal sites which determines their binding strength.<sup>68,69</sup> This electronic or ligand effect is often less dominant due to its indirect nature in affecting the interaction between metal sites and reactants/intermediates.

Besides the metal–ligand interaction, tethered ligands on a catalyst surface can directly interact with adsorbed  $\text{CO}_2$  molecules. For instance, Wang et al. demonstrated that tethered surface ligands with amine functional tail group (e.g., cysteamine) on Ag nanoparticles can facilitate the transition of physisorbed  $\text{CO}_2$  molecules to a chemisorbed state  $\text{CO}_2^{*+}$ , significantly enhancing catalytic activity for CO





**Figure 6.** Schematic illustration of the molecular modification approach. Molecular modifiers (e.g., nanocatalyst ligands) with various functional groups can be employed to manipulate their interactions with catalyst,  $\text{CO}_2$  molecules, intermediates, electrolyte ions, and water molecules, tuning the catalytic microenvironment of nanocatalysts. Functional groups at different positions of the molecular modifiers are highlighted by different colors (yellow, green, and blue).

production compared to their ligand-free counterparts.<sup>70</sup> This work signifies that nanocatalyst ligands can be utilized to provide unique reaction centers through ligand–intermediate interactions.

In addition to participating in reactant/intermediate stabilization, nanocatalyst surface ligands can be employed to regulate the availability of  $\text{CO}_2$  and water molecules to the catalyst surface which adjusts the composition of the regime confined near the particle surface. In the work by Pankhurst et al., organic ligands containing the imidazolium group were anchored on Ag nanocatalysts to favor the presence of  $\text{CO}_2$ .<sup>72</sup> Inspired by  $\text{CO}_2\text{RR}$  studies carried out in ionic liquid solutions, the imidazolium motif was predicted to interact strongly with  $\text{CO}_2$  molecules and increase their concentration near the catalyst surface. Additionally, the length of the ligand tail was further tuned to optimize the hydrophobicity at the ligand/electrolyte interface, promoting the  $\text{CO}_2$ -to- $\text{CO}$  electroconversion while suppressing HER.

Beyond the ligand tethering strategies, our group recently demonstrated that surface ligands (e.g., phosphonic acid) can also be utilized to create a favorable microenvironment between the metallic nanoparticle surface (e.g., Ag, Au, and Pd) and a structurally ordered ligand layer in a detached state.<sup>45</sup> This catalytic microenvironment where metal sites, electrolyte cations, and surface ligands work cooperatively was termed the nanoparticle/ordered-ligand interlayer (NOLI). At the  $\text{CO}_2$ -reducing bias, cations are inserted into the interlayer, stripping off their hydration shell. The desolvated cations associated with the vicinal anionic ligand layer, in contrast to fully hydrated cations found at a typical ligand-free metal catalyst surface, were found to facilitate the bending of adsorbed  $\text{CO}_2$  molecules through enhanced electrostatic interactions. This confined reaction environment is well maintained throughout  $\text{CO}_2\text{RR}$  by the stable ligand layer reinforced through intimate noncovalent ligand–ligand interactions.<sup>71</sup> This unique confined environment created near the active site enables a much improved catalytic turnover.

The concerted operation of the multiple components in the NOLI resembles the configuration of enzymes where an optimal microenvironment around the active site is achieved by amino acid side chains of the proteins, leading to superior catalytic reactivity and selectivity.<sup>73,74</sup> This study suggests that intricate interplays between surface ligands and the multiple constituents of the electrocatalytic interface are critical to create an enzyme-like microenvironment tailored for  $\text{CO}_2\text{RR}$ . Such a design model can be used to guide future nanocatalyst developments toward more comprehensive architectures mimicking that of enzymatic counterparts and achieve similar catalytic activity/selectivity targeted for  $\text{CO}_2$  electroconversion.

#### 4. CONCLUSIONS AND OUTLOOK

The electrocatalytic reaction conditions of  $\text{CO}_2$  electrolysis induce a variety of dynamic processes both *at* and *near* the catalyst surface, affecting both the catalyst structure itself and its local reaction environment. Throughout this Perspective, we have emphasized the significance of delving into catalytic active sites that exist *in situ* during  $\text{CO}_2\text{RR}$  accounting for the measured catalytic performance. *In situ/operando* spectroscopy and microscopy techniques will be pivotal to studying the dynamic structural transformation of nanocatalysts under  $\text{CO}_2$ -reducing conditions and identifying the catalytically active form of the catalysts. The impact of applied bias on the interaction of surface atoms with their core structure, their support, and surface-bound species, should all be examined to modulate their transition to their *effective/active* state during electrocatalysis. Improved understanding of this phenomenon and the catalytic property of the newly formed catalytic reaction sites will be necessary for the development of advanced nanocatalyst and also the future integration and optimization of nanocatalysts into high-rate operating conditions (e.g., electrolyzer applications). For instance, the controlled structural transformation of nanocatalysts at the three-phase boundary in gas-diffusion environments will be an important research direction to eventually attain industrially relevant performance.

Furthermore, the contribution of the microenvironment to the progress of  $\text{CO}_2\text{RR}$  should be considered in parallel with the evolution of the catalyst. The dynamic interactions between near-surface species, reactants, intermediates, and surface-bound species should be all accounted for in a comprehensive manner to efficiently isolate the parameters necessary to narrow down desired  $\text{CO}_2\text{RR}$  pathways. Overall, time and spatially resolved characterization techniques for nanocatalyst microenvironment studies need to be employed and further developed in order to circumvent the challenges of their dynamic and interactive nature during electrocatalysis. Structural dynamics should be concurrently monitored, or at least considered, with the characterization and data interpretation of near-surface species present during the reaction.

In this Perspective, we have specifically discussed tandem electrocatalysis (symmetric and asymmetric) and molecular modification (molecular modifiers interacting with  $\text{CO}_2$  reactants, intermediates, electrolyte ions, and water molecules) approaches to manipulating the catalytic microenvironment to control catalytic performance. Although these approaches have provided us with some valuable information extracted from experimental observations, the use of *in situ* and *operando* techniques remains the most reliable way to assess the contribution of the microenvironment to the measured

catalytic performance. These characterization capabilities have already provided essential insights and, with further development, will narrow down how the microenvironment formed under CO<sub>2</sub>-reducing conditions contributes to the observed catalytic performance.

Additionally, because microenvironments formed in typical aqueous conditions are not necessarily equivalent to those in high-rate conditions, more studies based on experimental approaches coupled with microkinetic modeling will be needed. In the future, accounting for the multidimensional nature of the catalytic interface formed at the surface of the nanocatalyst and evolving over the course of CO<sub>2</sub>RR will become inevitable to truly advance our targets of CO<sub>2</sub> valorization.

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### Notes

The authors declare no competing financial interest.

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