



# CO<sub>2</sub> turnover at the atomic interfaces, what's next?

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## ABSTRACT

Efficient and selective electrochemical CO<sub>2</sub> catalysis hinges on the facile CO<sub>2</sub> dissociation and the optimal binding energies of key reaction intermediates. However, optimizing these variables simultaneously poses a significant challenge, as the bindings of different intermediates are closely intertwined. Recently, single-atom alloys (SAAs) emerge as promising substances for catalytic applications that may provide a new approach to circumvent scaling relationships in electrochemical CO<sub>2</sub> reduction reactions (CO<sub>2</sub>RR). In this discussion, we emphasize the complementary roles of the host metal and dopant atoms in SAAs for CO<sub>2</sub>RR and discuss future outlooks for turning over the host and dopant relationship in SAAs for designing more efficient and selective catalysts for CO<sub>2</sub>RR.

## 1. Introduction

The electrocatalytic CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) presents a sustainable method for transforming greenhouse gases into valuable chemicals and fuels while simultaneously storing intermittent renewable energy. However, controlling the selectivity of CO<sub>2</sub>RR is a significant challenge due to the potential for producing at least 16 different gas or liquid products based on various reaction pathways [1]. This process is kinetically hindered by the involvement of multiple proton-coupled electron transfer steps, and it also faces competition with the thermodynamically more favorable hydrogen evolution reaction (HER) [2]. To achieve efficient CO<sub>2</sub>RR with specific target products, it is crucial to design and synthesize catalysts that have optimal bonding strength with key intermediates. Nevertheless, the adsorption properties of heterogeneous catalysts are often dominated by mean-field behavior [3], resulting from their wide electronic band structures. Consequently, current metal-based catalysts generally adhere to linear scaling relationships and cannot catalyze at the thermodynamic optimum, which imposes fundamental constraints on catalytic performance in terms of reactivity and selectivity.

To make the highly desirable CO<sub>2</sub>RR economically viable, researchers are looking for ways to circumvent the scaling relationships. One powerful method of adjusting a metal catalyst's properties is through alloying. The use of alloys in catalysis is not a new concept. In fact, the use of bimetallic catalysts dates back to the early 1900 s, when Sabatier and Senderens discovered that Ni and Pt alloys could catalyze the hydrogenation of organic compounds [4]. However, it was not until

the 1980 s and 1990 s that the use of alloys in catalysis gained more attentions, as researchers began to explore the potential of bimetallic and multimetallic catalysts for various applications [5]. Typically, alloys still follow certain scaling relationships, and one of the major challenges in designing bimetallic catalysts is controlling the distribution of the different metals in the nanoparticle for optimal catalysis. This problem was addressed in the early 2000 s when researchers began to explore the use of dilute alloy catalysts, which consist of only a small percentage of one metal in a host metal [6,7]. These dilute alloy catalysts were found to exhibit unique catalytic properties, and the development of single-atom alloys (SAAs) was a natural extension of this exploration. SAAs are composed of isolated metal atoms dispersed into the metal host. They exhibit distinguishable electronic and chemical properties than bulk metal, which can potentially provide high selectivity towards particular adsorption and desorption of intermediates during the CO<sub>2</sub>RR. The advancement of SAAs creates a novel approach to combine the best features of both heterogeneous and homogeneous catalysts. On the other hand, the idea of creating atomic interfaces also aims to tackle the structural intricacies of metal-nanoparticle/support interfaces by narrowing down the origin of the catalytic activity to the interaction between the host and a solitary, well-characterized, and isolated metal atom. This stands in contrast to many conventional heterogeneous catalysts, where an assortment of active sites on the metal nanoparticles could potentially catalyze unwanted side reactions. Further, the atomic interfaces in SAAs can be tuned at the atomic level, providing a high degree of control over the catalytic activity and selectivity. This could potentially offer unmatched selectivity and even

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surpass the activity that is challenging to attain with nanoparticle in a range of reactions.

In 2005, Goodman and co-workers demonstrated the significance of Pd dimers in the PdAu highly dilute alloy ( $\sim 0.07\%$  Pd) in catalysis [8,9]. Specifically, they found that dimers consisting of two non-contiguous atoms of Pd were the most active sites for the acetoxylation of ethylene to vinyl acetate. This discovery was a significant milestone in the development of SAAs, as it provided evidence that the presence of only a few isolated metal atoms in a host metal could significantly enhance catalytic activity. In 2009, Sykes and co-workers combined experiments and theory to demonstrate that isolated Pd atoms in Cu could activate  $H_2$ , which could then spill over to the Cu surface [10]. By 2012, they leveraged this catalytic property to selectively hydrogenate olefins at low temperatures [11]. This was another significant milestone in the development of SAAs, as it showed that isolated metal atoms in a host metal could act as active sites for catalytic reactions. These landmark studies paved the way for the steady development of what is now known as single-atom alloy catalysis. Shortly after the initial model catalyst demonstrations, many groups began to show that high surface area SAA catalysts can perform industrially important reactions including selective hydrogenations, C–C and C–O coupling reactions, alcohol dehydrogenations, C–H activation, and alkane dehydrogenations [12].

## 2. Turn over the host-dopant relationship in SAAs

In single-atom alloys, the general understanding is that the doped single atoms act as the primary active sites and are responsible for catalysis. This unique structural feature allows for greater flexibility in tailoring their electronic properties compared to monometallic counterparts, enabling better control over their catalytic activities. Single atoms in SAAs often display a lower density of state (DOS) near the Fermi level than bulk references, and their valence bands tend to be narrower, giving them a free-atom-like character [3]. Additionally, the *d*-band positions of single atoms can experience significant shifts. These changes in electronic structure greatly influence the adsorption behavior of adsorbates during catalytic processes [13]. However, recent studies showed that the host metal may also play a significant role in the electrochemical catalytic  $CO_2$  reduction process, either directly or as part of a cooperative mechanism (Fig. 1).

A recent study from our group presents a copper-catalyzed process for the exclusive conversion of  $CO_2$  into pure formic acid using single-atom alloying. We developed a copper-based SAA catalyst with isolated Lead (Pb) atoms doped into the copper matrix. The catalyst demonstrates remarkable performance, achieving 100% selectivity in the

electrochemical reduction of  $CO_2$  to formic acid [14]. We attributed this high selectivity to the synergistic effect between copper and the isolated Pb atoms in the SAA. The presence of isolated Pb atoms not only enhances the carbon protonation of  $CO_2$  to the copper surface but also increases the reaction barrier of oxygen protonation of  $CO_2$  to form the intermediate  $COOH^*$  and the competitive hydrogen evolution, resulting in the exclusive formation of formic acid. Attenuated Total Reflection Fourier-Transform Infrared (ATR-FTIR) spectroscopy was used to monitor the  $CO_2$ RR process on various catalysts (Fig. 2a). For the pure Cu catalyst, two infrared bands indicated the presence of  $^*CO$ , a key intermediate for C–C coupling and further hydrogenation (Fig. 2b). However, no  $^*CO$  bands were observed for the  $Pb_1Cu$  catalyst (Fig. 2c), suggesting substantial protonation of carbon in  $CO_2$  instead of oxygen protonation. The  $HCOO^-$  infrared band was detected at  $1384\text{ cm}^{-1}$  for the  $Pb_1Cu$  catalyst, which aligns with the  $1382\text{ cm}^{-1}$  band for pure Cu and differs from the  $1414\text{ cm}^{-1}$  band for Pb metal (Fig. 2c). The results suggest that formate intermediates are more likely adsorbed on Cu sites rather than isolated Pb sites in the  $Pb_1Cu$  catalyst, this is in line with the observations made through in situ Raman analysis (Fig. 2d). Additionally, density functional theory (DFT) calculations were conducted to understand the adsorption structures of  $HCOO^*$  on various sites, these calculations demonstrated that the Cu–Cu site in close proximity to Pb exhibited the most robust  $HCOO^*$  binding (as shown in Fig. 2e) and the highest  $CO_2$ RR activity for formate production (as depicted in Fig. 2f), in comparison to both the Pb-top site and the Pb–Cu co-ordinated site.

Moving beyond Pb, recent SAA works have also shown the possibility of shifting the  $CO_2$ RR toward CO production by promoting oxygen protonation of  $CO_2$  [15]. Specifically, Cu–Sn single-atom surface alloys ( $Cu_{97}Sn_3$ ), with isolated Sn sites anchored on the Cu host were reported. The  $Cu_{97}Sn_3$  catalyst demonstrates a high CO Faradaic efficiency of 98% at a minimal overpotential of 30 mV and a high CO current density of  $100\text{ mA cm}^{-2}$  at an overpotential of 340 mV in an alkaline flow cell, which leads to distinct catalytic selectivity compared to pure  $Cu_{100}$  and  $Cu_{70}Sn_{30}$  bulk alloy. Although DFT simulations did not specify the exact active sites, they reveal that the electrocatalytic reactivity of Cu–Sn alloys is not solely determined by their elemental composition; rather, the local coordination environment of atomically dispersed isolated Cu–Sn bonding plays a crucial role. The PDOS of Cu *d* orbitals in surface alloy exhibits a noticeable shift to the left compared to that of pure Cu, resulting in the *d*-band center being positioned 0.1 eV further from the Fermi level than in pure Cu. Consequently, the bondings of  $COOH^*$ ,  $H^*$ , and  $OCHO^*$  are weakened on isolated Cu–Sn bonds, which is believed to be advantageous for CO generation.

An additional study reported an antimony-copper single-atom alloy

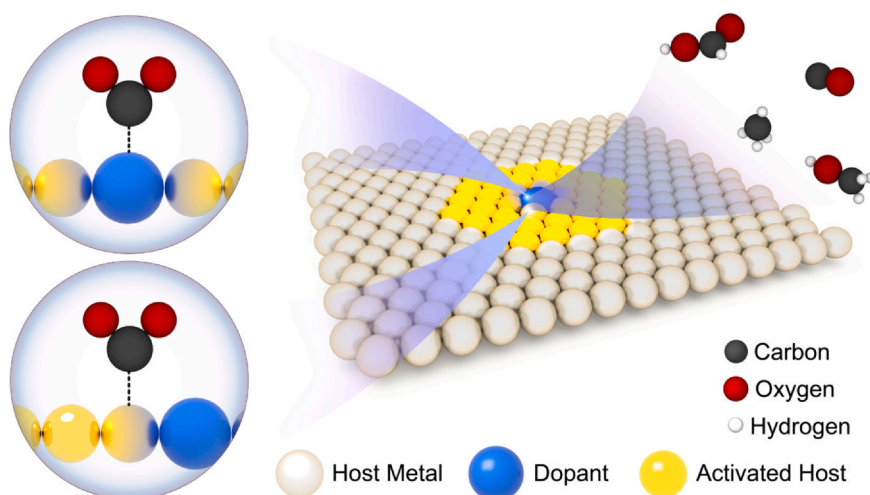
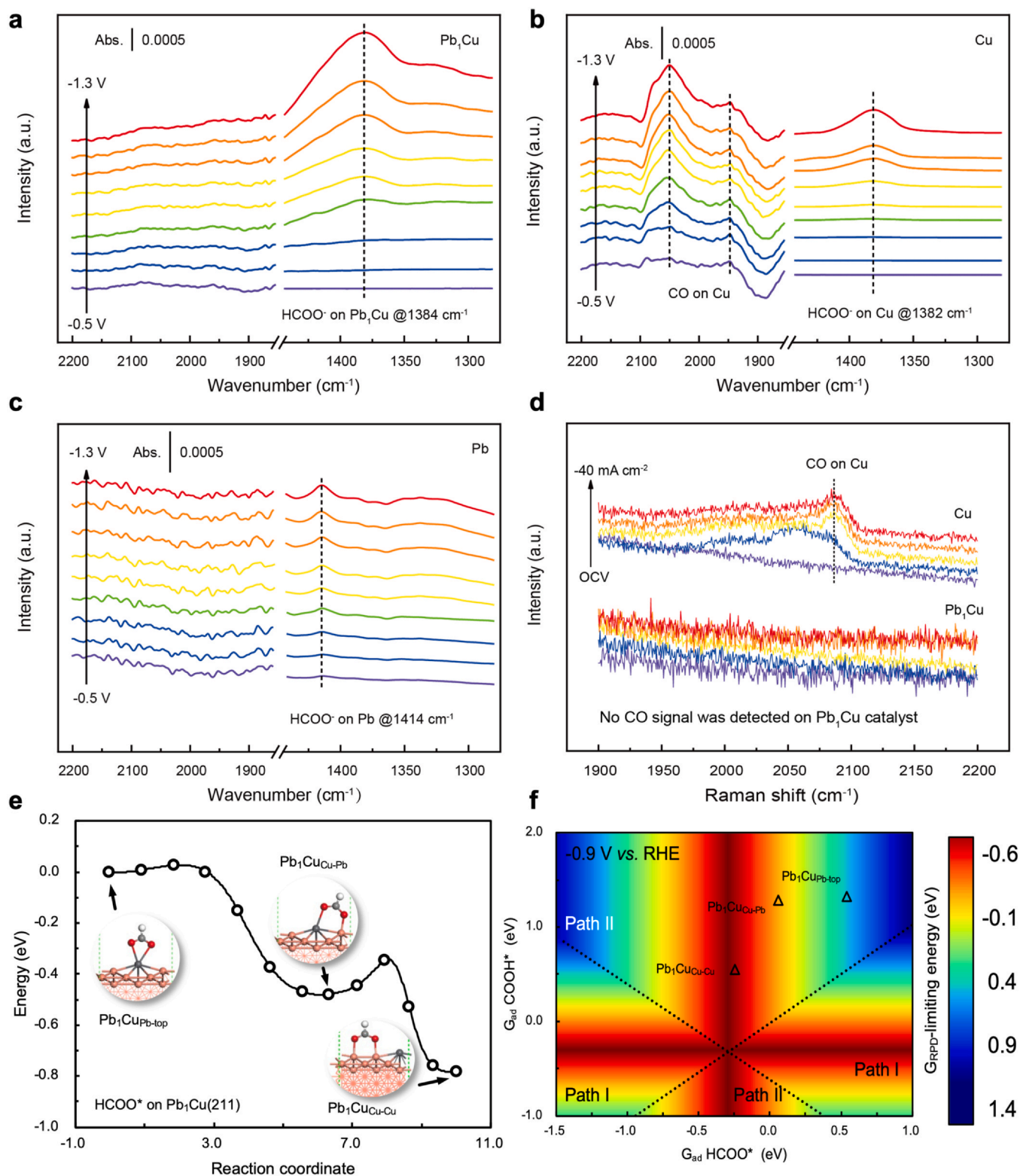


Fig. 1. Schematic showing two possible catalytic mechanisms mediated by SAAs.  $CO_2$  absorption and intermediate desorption become both available on dopant-modulated host metals, or reversely.



**Fig. 2.** (a–c) In situ ATR-FTIR spectra recorded at different applied potentials for the Pb<sub>1</sub>Cu SAA (a), pure Cu nanoparticles (b), and Pb nanoparticles (c). (d) Raman spectra were recorded in situ at varying current densities for Cu and Pb<sub>1</sub>Cu single-atom alloy (SAA) catalysts, demonstrating that CO formation did not occur on the Pb<sub>1</sub>Cu catalyst. (e) DFT results comparing energy alteration during the transfer of HCOO\* from the Pb-top site to Pb-Cu and Cu-Cu sites on Pb<sub>1</sub>Cu. (f) Two-dimensional reaction phase diagram that demonstrates the activity of CO<sub>2</sub>RR in generating formate across different active sites on Pb<sub>1</sub>Cu. The dotted lines represent the more favored reaction paths, where path I represents the COOH\* path and path II represents the HCOO\* path.

catalyst (Sb<sub>1</sub>Cu) with isolated Sb-Cu interfaces, which was developed to efficiently convert CO<sub>2</sub> to CO, achieving a Faradaic efficiency of over 95% [16]. In situ spectroscopic measurements and theoretical simulations reveal that the local electronic and geometric configuration of Cu

was fine-tuned to inhibit C-C coupling without reducing intrinsic activity, thus addressing the CO activity-selectivity dilemma on Cu. The atomic Sb-Cu interface in Cu is believed to enhance CO<sub>2</sub> adsorption/activation and weakens the binding strength of \*CO intermediates,

resulting in improved CO selectivity and production rates. DFT calculations were carried out to comprehend the enhanced CO faradaic efficiency, based on the premise that CO adsorption sites are located on the Cu sites. The results revealed that the  $^*CO$  adsorption energy at the top site on Cu (next-nearest to the Sb atom,  $-0.21$  eV) was nearly identical to that of pure Cu ( $-0.20$  eV), and more stable than  $^*CO$  at the top site of Cu (closest to the Sb atom,  $-0.11$  eV). When combined with the findings from spectroscopic observations, which indicate a weaker  $^*CO$  adsorption due to the reduced frequency of the  $^*CO$  peak on  $Sb_1Cu$  than Cu, it can be inferred that the Cu sites closest to the Sb atom on  $Sb_1Cu$  have a crucial role in enhancing the overall activity.

In contrast to the traditional activate-spill concept in SAAs, the examples mentioned earlier introduce the novel concept of SAAs, in which a host material is locally activated by single-atom doping, potentially enhancing the  $CO_2RR$  activity and selectivity. This design offers several benefits compared to traditional single-atom catalysts. Firstly, although single-atom catalysts exhibit remarkable activity per metal atomic site, they suffer from low metal-atom densities, limiting their overall catalytic performance. By turning over the host-dopant relationship, higher current densities of the catalyst can be achieved. For instance, the  $Pb_1Cu$  catalyst demonstrated an outstanding FE of 96% with a current density of  $800\text{ mAcm}^{-2}$ , outperforming previously reported formic acid electrocatalysts. And the catalyst exhibits excellent stability and durability, maintaining its performance for over 180 h of continuous operation. Secondly, single sites are incapable of driving multi-electron/multi-proton transfer steps and C-C couplings, while a doped host does not suffer from this limitation. Lastly, single-atom catalysts tend to exhibit poor stability as they can easily aggregate during the reaction to minimize surface energy. However, if these single atoms are inert toward the reactant or engaged with the host in an intense mutual interaction, their stability can be significantly improved.

In the realm of novel catalyst design for catalytic reactions, an appreciation of the intricate relationship between the structure and performance of SAAs at the atomic level is of paramount significance [17–20]. The variations in SAA structures can be compartmentalized primarily into several key facets. The first of these involves the phenomenon of lattice distortion. It is caused by the differences in the lattice constants of two metals, influencing the bond strength of intermediate as a long-range effect. The strain effects are reflected by the change in the metal bond length. Besides, the strains may be different in disparate directions, which is due to the atomic packing modes in unit cell. Meanwhile, the charge transfers due to the differences in electronegativity as a short-range effect, also alters the electronic structures and leads to the variation in binding strength of intermediate. Secondly, the atomic distance - specifically alterations in the spacing between two individual atoms post alloying—has a fundamental influence on the mode of adsorption of intermediate entities on a variety of atomic assemblages. Take for instance the case of CO adsorption on Pd. Experimental observations have demonstrated a diminution in CO's binding strength on Pd as it transitioned from a hollow to a linear configuration, which correlated with the occupation of multi-continuous Pd sites and singular Pd sites respectively [10]. This suggests that the adsorption capacity of CO on Pd can be modulated by manipulating the cluster size of Pd atoms. It can be extrapolated that when the concentration of surface dopants escalates, the parent metal segregates into progressively smaller granules. This phenomenon could potentiate the optimization of the reaction path and could enhance the selectivity towards desired products. The coordination number, as well, exhibits a tangible impact on catalytic outcomes. For instance, research conducted by Calle-Vallejo and colleagues provides empirical evidence that the catalytic activity for CO oxidation on Pt follows a trajectory of initial increase, succeeded by a decline, in tandem with a diminishing coordination number. [21] Alterations to the local coordination number within SAAs can be brought through the introduction of vacancies or defects, as well as adjustments to the particle size of the host metal. This indicates a potential pathway for modulating catalytic activity by

strategically manipulating the coordination number within SAAs. Overall, the cumulative effect on the adsorption property is predicated upon the synergistic interplay of the aforementioned factors. By judiciously managing the composition and variety of alloy elements, there exists great potential to optimize the catalytic performance.

### 3. What's next?

The idea of turning the host metal or the single atom/host interfaces in SAAs into active sites is a promising approach for developing efficient and selective catalysts. The tuning of the electronic properties of the host metal by incorporating the single atoms can enhance the catalytic performance by creating new active sites and modifying the reaction pathways. Introducing a third or even more components could further diversify the catalytic landscape, potentially enabling more nuanced interactions and synergistic effects. This approach could, hypothetically, allow for the fine-tuning of catalytic activity and selectivity, thereby breaking linear scaling relationships that are typically observed in simpler systems. Moreover, Cao et.al recently presents the inaugural evidence that a single-atomic Bi decorated Cu alloy can potentiate the C-C coupling process, [22] concurrently enhancing the selectivity of electrocatalytic  $CO_2RR$  towards the production of  $C_2+$  products. According to their DFT calculations, the Bi sites do not function as active sites but rather serve in the capacity of a promoter or modifier, causing alterations in the electronic structure of the copper. This innovative approach heralds new potential for the design of highly effective and durable SAAs for  $C_2+$  products. Here we briefly outline the further research and development direction in this area, aiming to provide new opportunities for designing and optimizing SAAs for various catalytic applications besides  $CO_2RR$ .

First of all, distinguishing single atoms in SAAs can be a challenging task due to the limitations of existing characterization techniques. The challenge lies in identifying and characterizing the single atoms in the alloy and understanding their interaction with the host metal. Determining whether adsorbates adhere to the dopant, the host material, or through their combined interaction is also essential for unraveling the catalytic mechanisms of these materials. Traditional transmission electron microscopy (TEM) can only provide atomic-scale resolution for high-Z elements, while X-ray absorption spectroscopy (XAS) has difficulty differentiating between single atoms and small clusters. It can also be difficult to ensure that the alloy maintains the truly single atoms in a dynamic atmosphere, as the presence of clusters or nanoparticles can be formed and greatly affect the properties and performance of the catalyst during the reducing conditions. Furthermore, the distribution of single atoms within the host material can also be uneven, making it difficult to identify and characterize the single-atom sites with certainty. Moreover, when these single atoms are close enough to each other, a redistribution of charge occurs, resulting in the creation of distinct new active sites. Therefore, the development of new, more advanced techniques for characterizing individual single-atom sites and inter-site distance effects is essential for gaining a deeper understanding of their properties and potential applications in catalysis. It is broadly acknowledged that no single method is entirely sufficient in confirming the atomic dispersion or local environment of a single-atom catalyst. Instead, it's necessary to utilize information from at least two or, ideally, multiple techniques to obtain a comprehensive understanding, given that each individual method has its own limitations. Moreover, it is crucial to conduct smart in situ studies in addition to pre- and post-reaction characterizations, to comprehend how the surface structure evolves under reaction conditions. For instance, CO is a crucial intermediary in numerous  $CO_2RR$  pathways. The vibration frequency of CO is influenced by the metallic elements involved, and adsorbed CO on single, double, and triple sites exhibits distinct vibration frequencies. By utilizing infrared spectroscopy to analyze the adsorption/desorption behavior of CO, valuable insights can be obtained regarding the types of surface sites and the conformations of CO



adsorption. In cases where the  $^*\text{CO}$  peak is not easily distinguishable, other vibrations can be carefully examined to provide additional information. For example, our previous example shows that  $\text{HCOO}^-$  infrared band can be potentially used to determine the active site in the  $\text{Pb}_2\text{Cu}$  catalyst.

Second, the development of metal catalysts, including monometallic and intermetallic catalysts, has seen significant advancements due to descriptor-based linear scaling relationships. These relationships help in understanding and predicting the performance of catalysts based on a few key parameters. Some of these relationships include thermochemical scaling relationships, Brønsted–Evans–Polanyi (BEP) relationships, the  $d$ -band model, and generalized coordination numbers. These simple models have been particularly useful for experimentalists and theoreticians in rationalizing experimental observations and making on-the-fly predictions during multiscale modeling simulations. However, the behavior of SAAs can differ significantly from that of pure metals, largely due to their unique electronic structure. Previous studies have assumed that the catalytic sites for SAAs are diluted single atoms, and the electronic structure of SAAs has been compared to that of gas-phase atoms, which explains their distinct behavior. Consequently, further investigation and development of new models may be needed to improve our understanding and prediction of these materials' performance. Notably, a critical reassessment of the established relations, with an intensified focus on the host material as the focal point of investigation, might yield deeper insights and more accurate predictive measures for the performance of these materials.

The industrial adoption of SAAs depends on the successful scale-up and long-term stability of the catalysts in dynamic industrial environments. Typically, recognized procedures like galvanic replacement [23–25], sequential reduction [26,27], and incipient wetness co-impregnation [28,29] have been established as dominant methodologies within the current scientific dialogue regarding SAA production. Additionally, other methods including strong electrostatic adsorption [30], controlled surface reaction [31], electroless deposition [32], and co-reduction [33] have been reported, further expanding the toolbox available for SAA synthesis. Some of them are particularly attractive for producing large quantities of catalysts, as evidenced by the recent development of a ball milling procedure suitable for kilogram-scale production [34]. Stability is a critical factor for SAAs, as it determines their suitability for various industrial applications. The aggregation energy serves as an indicator of the tendency for dopant atoms in SAA to remain dispersed as isolated entities within the host material or cluster together. When SAAs are successfully synthesized, it invariably implies that the energy of aggregation is positive. A prime example is the NiCu SAA system, which offers a cost-effective and environmentally friendly catalyst for nonoxidative ethanol dehydrogenation to acetaldehyde and hydrogen, outperforming pure Cu in terms of stability while retaining high selectivity [35]. This thermodynamic force is key in fostering isolation of sites, a factor that is crucial in reducing problems such as clustering or sintering that are frequently experienced in different types of single-atom catalysts. Interestingly, Sun and his team discovered a remarkable stability issue in PtCu SAA when used for propane dehydrogenation [36]. Post-reaction analysis of the catalyst revealed that even the catalyst was heated to 600 °C, the Pt sites remained separate. However, they noticed that the Cu host nanoparticles began to coalesce, which suggests that the issue with SAAs currently may not be the stability of the individual atom sites but the nanoparticles themselves. Specifically, the sintering and leaching of the Cu host nanoparticles, rather than clustering of the isolated Pt atoms, is what causes deactivation at higher temperatures or harsh electrochemical conditions. To counter this problem, strategies for maintaining the stability of the host nanoparticles to prevent sintering may be applied, such as size engineering [37], atomic layer deposition (ALD) coating [38], and securing them within a carbon matrix [39].

Theoretical calculations and computational methods have been increasingly employed in the field of electrocatalysis to design and screen

potential catalysts for specific electrochemical reactions. These methods offer advantages over the traditional trial-and-error approach, which can be cumbersome, complicated, and labor-intensive. For example, DFT calculations and microkinetic methods have been applied to screen the optimal dopant on Cu for  $\text{C}_2\text{H}_4$  production [40]. A high-throughput compressed-sensing data-analytics approach parameterized with DFT inputs has also been applied for the prediction of the catalytic performance of thousands of SAAs in hydrogenation reactions [41]. Given the extensive design possibilities, machine learning is another potential candidate to become a crucial instrument as soon as adequate training data sets are developed. This advancement would also facilitate progress by gathering data on the energetics of elementary steps that occur at each active site. As a result, researchers can expand their investigations beyond bimetallic systems and examine complex pathways. For example, Dasgupta *et al.* employed a new computational framework in the machine learning method to predict reaction and adsorption energies for 300 SAAs [42], which helped pinpoint potential active materials that do not conform to the scaling relationship. Although considerable advancements have been made to investigate descriptors for screening potential SAAs across various reactions, coherent models are expected to be developed specifically for SAAs with active host metals in the electrocatalytic process.

## Author contributions

All authors have made a substantial, direct, and intellectual contribution to the work and approved it for publication.

## Declaration of Competing Interest

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

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