ACS MATERIALS Au
AN OPEN ACCESS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

pubs.acs.org/materialsau
Perspective

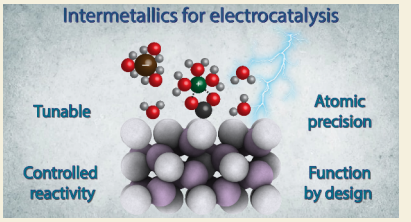
The Essential Role of Well-Defined Materials in Assessing Electrocatalyst Structure and Function

Published as part of ACS Materials Au special issue "2024 Rising Stars".

Anthony Shoji Hall*

Cite This: *ACS Mater. Au* 2025, 5, 231−238
Read Online
ACCESS | Metrics & More | Article Recommendations

ABSTRACT: Advancements in heterogeneous electrocatalysis are essential for the transition to a sustainable future. However, current catalysts often face limitations in activity, selectivity, stability, and cost-effectiveness, highlighting the need for a detailed understanding of catalyst behavior to construct rational design strategies. This perspective focuses on the role of well-defined materials, particularly ordered intermetallics, in enhancing catalytic performance. Ordered intermetallic materials enable precise control over geometric and electronic properties, which are critical for tailoring reactivity. Their structured atomic configurations not only allow for rational control of catalytic activity but also integrate seamlessly with computational models, facilitating the design of improved materials. Additionally, we examine future research directions for intermetallics in electrocatalysis, identifying opportunities for significant breakthroughs in the field.



KEYWORDS: *Intermetallic Electrocatalysts, Structure−Property Relationships, Catalyst Design Strategies, Active Site Engineering, Artificial Intelligence in Catalysis, Sustainable Energy Materials, Alloys*

INTRODUCTION

The energy transition hinges on developing advanced electrochemical devices designed to efficiently store and convert renewable electricity to and from energy dense small molecules (e.g., hydrogen, ethanol, etc.).[1] Key devices include fuel cells, which convert chemical energy into electricity, and electrolyzers, which store electricity in chemical bonds.[1,2] Electrified metal-solution interfaces are critical, as the properties of the components in this interface influence the behavior and efficiency of electrochemical reactions.[3]

Metal electrodes are an essential part of electrochemical devices as they mediate bond breaking and bond formation alongside electron transfer. However, single-element metal electrodes often exhibit limitations in selectivity and activity, necessitating the exploration of methods to enhance their reactivity.[4] Alloying is a prevalent strategy to enhance the performance of metals catalysts.[4−12] This approach modulates the electrochemical behavior by three mechanisms: ensemble effects, ligand effects, and strain effects.[13−15] The ligand effect describes changes in the electronic structure of the material from alloying, as the constituent components typically have different electronegativites.[14,16,17] The ensemble effect involves alterations in chemisorption properties from changes in the configuration of the adsorption site (i.e., ensemble), which can modify the binding geometry of adsorbates on the surface.[13,18] The strain effect pertains to changes in bond lengths from variations of the lattice constants, which alter the material's electronic structure and influences how adsorbates interact with the surface.[14] In particular, the ensemble effect dictates the configuration of the active site, while the d-band theory developed by Norskov et al. explains how variations in the material's electronic structure regulate the adsorption energy of reaction intermediates and spectator species.[19] Although the theoretical framework for catalyst design is well-established, the rational design of materials with precise control over both geometric and electronic properties remains challenging.

In this Perspective, we will discuss advances in the use of ordered intermetallic materials (hereafter referred to as intermetallics)—an underutilized class of materials in catalysis research—that offer an excellent platform for detailed interrogation of structure−property relationships. By leveraging their well-defined structures, intermetallics enable precise control over both geometric and electronic properties, making them invaluable for understanding and optimizing catalytic performance. We highlight current trends and share our views on future directions for the field of heterogeneous electrocatalysis.

Received: September 1, 2024
Revised: December 3, 2024
Accepted: December 9, 2024
Published: December 23, 2024

https://doi.org/10.1021/acsmaterialsau.4c00105
ACS Mater. Au 2025, 5, 231−238

The Need for Atomically Defined Materials

Effectively controlling both the configuration of active sites and the adsorption energies of reaction intermediates is essential for developing advanced catalyst materials. Bimetallic and multimetallic alloys, which initially gained prominence in heterogeneous catalysis, are now a major focus in electrocatalysis research. This approach involves altering the identity and composition of elements within the alloy to influence catalyst behavior.[19,20] While this method has identified some high-performance catalysts, the rationale behind the selection of alloy components is often unclear. What initial considerations guide the selection of elements for an alloy? Frequently, it seems that compositions are discovered by a trial-and-error approach, with explanations created afterward to justify the findings. This Edison-like approach can yield valuable results, but it is inefficient. It relies on chance rather than systematic understanding, offering limited guidance for future catalyst development.

These challenges may arise because standard materials design strategies inadvertently alter multiple material attributes simultaneously. For instance, changing the composition of a solid-solution alloy will usually modify both the catalyst's active site geometry (i.e., ensemble) and its electronic structure, rendering the isolation of a singular effect difficult.

The active site on a heterogeneous solid is dependent on the configuration of atoms on the surface. For elemental metals the active site is controlled by cleaving the crystal at a specific orientation or by synthesizing shape-controlled nanoparticles to expose a desired facet.[3] This allows for the preparation of surfaces with specific ensemble sizes; for instance, six-coordinate atomic clusters can be obtained on the (111) facet, while five-coordinate atomic clusters are obtained on the (100) facet of an Face-centered cubic (FCC) crystal. In contrast, the active site structure in alloys is more complex. In solid-solution alloys it is commonly assumed that the surface consists of a random mixture with elements distributed indiscriminately. However, this view is too simplistic.[21] Even within alloys that are compositionally identical and share the same facet, the geometric configuration of atoms on the surface can vary significantly depending on the synthesis protocol employed.[22] This phenomenon is evident in the case of $Pd_3Fe(111)$ single crystals, where different annealing treatments significantly alter the surface configuration of the atoms.[22] For example, annealing at 1200K induces Pd atom segregation, resulting in the formation of Pd monomer and dimer adatoms on the surface, while annealing at 1000K produces a more randomized surface configuration (Figure 1). Moreover, alloys may undergo surface reconstructions, some of which lead to local chemical ordering driven by surface energy minimization.[23]

The fact that surfaces of single crystals of solid-solution alloys can adopt various structures suggests that nanomaterials, which are commonly used in electrocatalysis, can also exhibit diverse active site configurations on their surfaces. The complexity of nanomaterial alloy surfaces surpasses that of single crystal surfaces due to the vast parameter space involved in synthesis, including the presence of surfactants, solvents, and reducing agents.[21,24] Unlike bulk crystal surfaces, nanomaterial surfaces are challenging to characterize, as their smaller size and high surface complexity complicate precise determination of active site configurations. These variations in surface structure can have significant implications in catalysis, as materials with the same composition may exhibit different reactivity depending on how it was made from variations in the configuration of the active site.

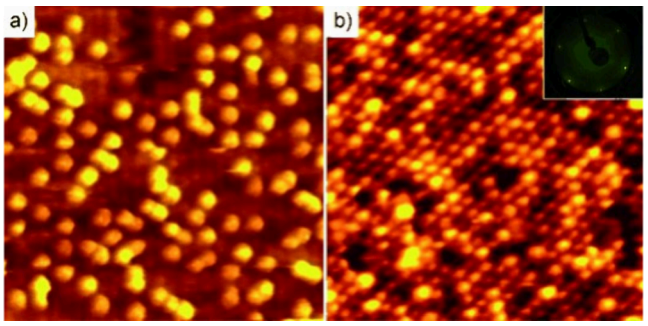


Figure 1. Constant-current scanning tunneling microscopy (STM) topography images of clean Pd_3Fe (111) single crystal alloys. a) Surface after heating to 1200 K showing the presence of Pd monomer and dimer adatoms (bright spots). b) Surface after annealing to 1000K showing a terrace with well-mixed atoms. Inset: low-energy electron diffraction pattern. Figure reproduced with permission from ref 22. Copyright 2011 WILEY-VCH Verlag GmbH and Co. KGaA, Weinheim.

One promising approach to address the limitations of traditional solid-solution catalysts is to use atomically well-defined systems, such as ordered intermetallic materials. Ordered intermetallics are a subclass of alloys composed of two or more metals, defined by fixed composition, fixed atomic positions and site occupancies which establish long-range atomic-scale order (Figure 2). In contrast, solid-solution alloys display a random distribution of elements within the bulk lattice, resulting in less predictable atomic arrangements and behaviors. This long-range atomic-scale order in intermetallics establishes a framework for precise control and predictability, which is crucial for advanced catalysis.

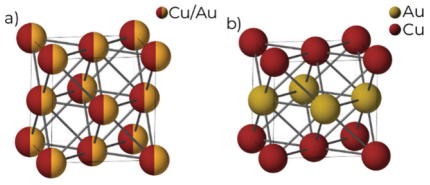


Figure 2. a) Unit cell of solid-solution CuAu alloy illustrating an equal likelihood of Au or Cu occupying each site, with a probability of 50% for either element. b) Unit cell of an ordered intermetallic AuCu alloy demonstrating long-range atomic ordering with specifically designated site occupancies.

Intermetallic materials, although ordered within the bulk, can display a variety of surface structures—from simple bulk terminations to complex reconstructions that deviate significantly from the bulk configuration. For instance, Al_5Co_2 (001) displays a $(\sqrt{3} \times \sqrt{3})$ R30° surface reconstructions, this surface deviates from what would be expected from a bulk-terminated crystal.[25] Additionally, the clean Ni_3Al (111) surface has been found to contain unexpected disorder at the surface, despite the bulk's ordered arrangement.[26] In contrast, FeAl (110) displays a surface structure that closely mirrors a bulk-terminated configuration.[27] These observations demonstrate that intermetallic materials have the potential to exhibit surface structures that either closely mirror the ordered bulk termination or differ significantly due to surface reconstructions.

https://doi.org/10.1021/acsmaterialsau.4c00105
ACS Mater. Au 2025, 5, 231−238

While intermetallics offer significant advantages for studying structure−property relationships, it is important to recognize their limitations compared to solid-solution alloys. Intermetallics are often constrained to specific stoichiometric compositions that support stable ordered structures, restricting the ability to extensively fine-tune electronic properties by varying composition. In contrast, solid-solution alloys allow for continuous variation in composition over a larger range, enabling broader exploration of electronic tunability at the expense of structural precision. Nevertheless, intermetallics remain invaluable for investigating fundamental structure−property relationships. Their ordered nature provides a more predictable framework compared to solid-solution alloys, allowing for more systematic studies of how structural variations affect catalytic behavior. This makes intermetallics superior for foundational studies, despite possible variations in surface structure. However, caution is necessary, as the surface of the material may differ from the bulk if surface energy minimization drives reconstruction. This aspect is often not thoroughly probed in many heterogeneous catalysis studies, highlighting the need for careful characterization of both bulk and surface structures.

Leveraging Structural Variability in Intermetallics for Tailored Catalytic Sites

The versatility of intermetallics provides a flexible platform for designing active sites with specific catalytic properties. In the following examples, we explore how subtle structural variations in intermetallic compounds—whether through polymorph selection or controlled atomic substitution—can drastically impact catalytic activity and selectivity. These examples display the potential of intermetallics as model systems for catalyst design.

Exploring different polymorphs of an intermetallic offers a strategic method to modify the configuration of the active site. Take Pt_3Zr, for instance, which can crystallize in various structures, including an FCC phase or a hexagonal closed packed (HCP) phase, depending on the annealing temperature of the alloy (Figure 3). The FCC Pt_3Zr, belonging to the space group $Pm\bar{3}m$, has a higher symmetry than the HCP Pt_3Zr, which crystallizes in the space group $P6_3/mmc$. This structural difference directly influences the configuration of the active site. Consequently, the hexagonal Pt_3Zr displayed ∼2× higher activity (on a surface-area normalized basis) for ethanol electro-oxidation compared to its cubic counterpart.[28] Although there is a difference in particle sizes between the cubic (100 nm) and hexagonal (200 nm) Pt_3Zr samples, the similar surface-to-volume ratios at these length scales suggest that particle size effects are minimal and do not significantly impact the results. The authors noted that this increase in activity was from an increased surface energy, while the stability of the catalyst was maintained by a lower bulk-free-energy. A review of the transmission electron microscopy (TEM) images showed no clear evidence of surface reconstructions in the Pt_3Zr samples, suggesting that the Pt_3Zr surfaces possess stable structures consistent with bulk terminations. This study highlights the significant impact that slight structural variations to the active site can have on catalyst behavior.

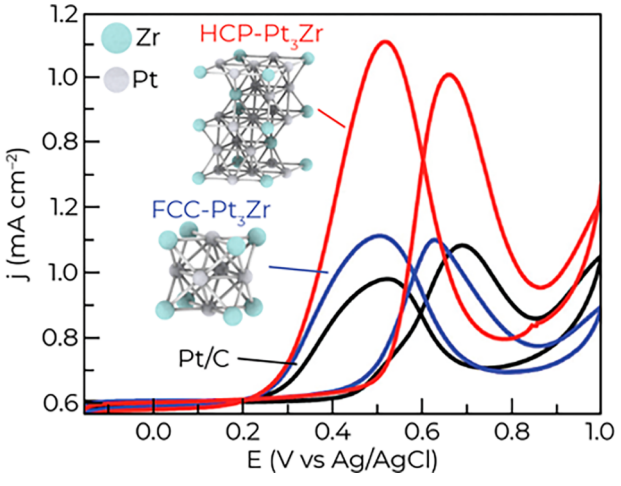


Figure 3. Ethanol electro-oxidation on Pt/C (black lines), cubic Pt_3Zr (blue lines), and hexagonal Pt_3Zr (red lines) catalysts. Inset images depict the crystal structures of hexagonal Pt_3Zr (top) and cubic Pt_3Zr (bottom). Figure adapted from ref 28. Copyright 2014 American Chemical Society.

Another strategy involves modifying the active element in an intermetallic by partial substitution, thereby altering the active site configuration. A recent study manipulated the composition of the γ-brass phase of Pd−Zn intermetallic, adjusting the composition from Pd_8Zn_{44} to $Pd_{10}Zn_{42}$ (∼4% difference in composition).[29] By leveraging the predetermined crystallographic sites within the γ-brass phase of the Pd−Zn intermetallic structure, Pd addition displaced adjacent Zn atoms in the octahedral sites, enabling the engineering of distinct active sites.

In the higher Pd-content compositions, such as $Pd_{10}Zn_{42}$ and Pd_9Zn_{43}, the introduction of additional Pd atoms occupies octahedral sites, forming Pd_3 trimers on the surface of the crystal (Figure 4a). In contrast, the Pd_8Zn_{44} composition, where all eight Pd atoms occupy only tetrahedral sites, results in isolated Pd_1 monomers surrounded by Zn atoms (Figure 4b). The Pd_9Zn_{43} serves as an intermediate composition that contains both Pd_1 monomers and Pd_3 trimers, bridging the gap between Pd_8Zn_{44} and $Pd_{10}Zn_{42}$ (Figure 4a). These Pd_3 trimers provide sufficient ensembles to effectively bind and activate acetylene and hydrogen, leading to a significant increase in activity for fully hydrogenating acetylene (C_2H_2) to ethane (C_2H_6). The Pd_1 monomers from Pd_8Zn_{44} are completely inactive for fully hydrogenating acetylene to ethane due to their inability to effectively coadsorb both reactants. Instead, Pd_8Zn_{44} displays high selectivity for the partial hydrogenation of acetylene to ethylene (C_2H_4). Pd_9Zn_{43}, with a mixture of Pd_3 trimers and Pd_1 monomers, displays intermediate activity. Although this method was initially applied in thermal catalysis, it holds promise for adaptation in electrochemical reactions as well.

Systematic Modulation of Electronic Structure and Active Site Configuration of Alloy Catayst

Precisely controlling both the configuration of active sites and the electronic structure of a catalyst is essential for optimizing catalytic performance. However, the use of solid solution alloys typically precludes such precise control, as adjustments to the alloy's composition concurrently alter ligand, strain, and ensemble effects. This is a consequence of Vegard's law, which states that the lattice constant of a solid solution varies linearly with composition, affecting the average bond lengths within the system.[30] Additionally, the electronic structure is modified because the constituent elements in the alloy generally possess different electronegativities, which significantly impact catalysis by altering the adsorption energies of reaction intermediates.[19] Consequently, current methods centered around the use of

https://doi.org/10.1021/acsmaterialsau.4c00105
ACS Mater. Au 2025, 5, 231−238

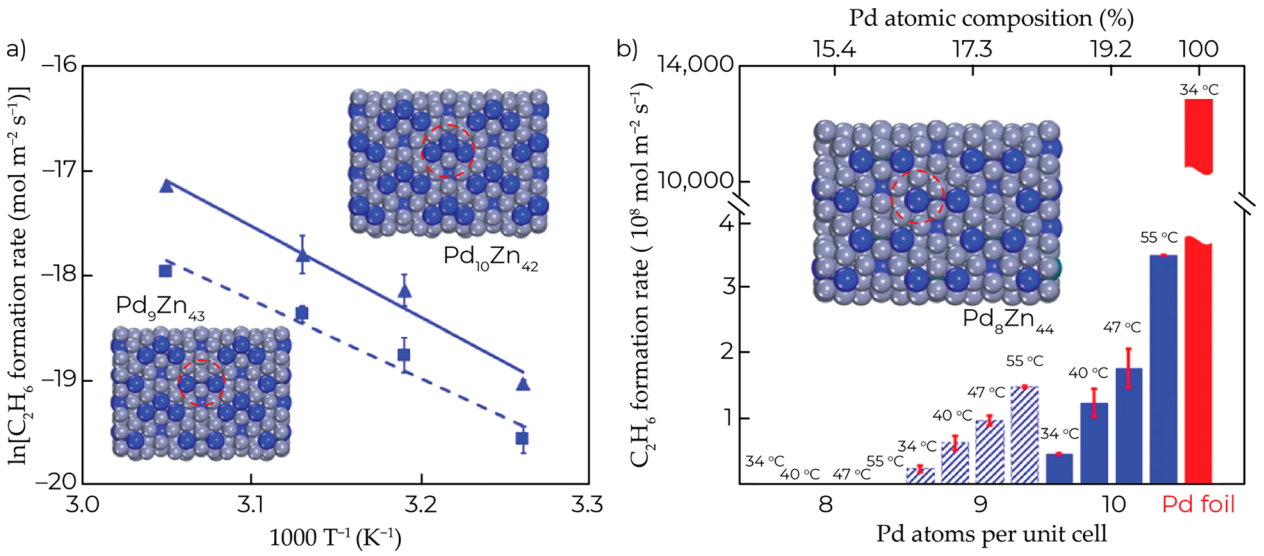


Figure 4. (a) Arrhenius plot for acetylene hydrogenation showing the temperature dependence of C_2H_6 formation on Pd_9Zn_{43} and $Pd_{10}Zn_{42}$ γ-brass phase intermetallics. The Pd_3 trimers exhibit significantly higher hydrogenation rates than isolated Pd monomers. Insets show representative atomic models of the Pd−Zn intermetallic structures, with Pd atoms (blue) and Zn atoms (gray) arranged in their crystallographic sites. (b) C_2H_6 formation rates from acetylene hydrogenation at various temperatures (34 °C, 40 °C, 47 °C, 55 °C) as a function of Pd atomic composition per unit cell. Increasing the Pd content from 8 to 9 atoms per unit cell shifts the active site configuration from isolated Pd monomers to Pd_3 trimers, resulting in a marked increase in activity for full hydrogenation. Pd foil data are included for comparison, showing the high activity of bulk Pd. The red dashed circles in the crystal structure insets of panels (a) and (b) show how the change in composition tunes the Pd sites from isolated sites to trimer sites. Figure adapted from ref 29. Copyright 2022 Springer Nature.

solid-solution alloys lack the capability to maintain the configuration of the active site while modulating the electronic structure.

Intermetallics offer a promising solution to this challenge by allowing the configuration of the active element to remain fixed while varying the identity of the inert element to modify the electronic structure. This elegant strategy was recently employed by leveraging the use of ternary intermatallics. In this approach $InPd_2$ and $SnPd_2$ alloys were combined to form a ternary $In_{1-x}Sn_xPd_2$ alloy.[31,32] Because both $InPd_2$ and $SnPd_2$ adopt the Co_2Si-type crystal structure, the Pd occupies its own sublattice, while the metalloid (In or Sn) occupies the other sublattice of the crystal (Figure 5). This strategy allows for the substitution of Sn into the In sublattice (or vice versa) while keeping the Pd sublattice intact. As a result, the valence electron concentration of the compound can be fine-tuned with minimal changes to the geometric configuration of the active element (Pd in this case), since Pd remains fixed in its sublattice. Moreover, the similar atomic diameters of In and Sn minimize strain effects by maintaining the interatomic distances at the active site.

This strategy can be further extended to systematically alter the interatomic distances within the active site while maintaining their relative positions by selecting substituting elements with different atomic sizes. For example, substituting Ga into the lattice of $InPd_2$ to form $Ga_{1-x}In_xPd_2$ changes the interatomic distances within the active site while maintaining the valence electron count of the compound, allowing for systematic probing of the strain effect via modulating the interatomic distance of the lattice (Figure 5).[31] Ga is suitable for this approach because $GaPd_2$ also adopts the Co_2Si crystal structure, but with a different lattice constant. Additionally, substituting Ga into the $SnPd_2$ system to form $Ga_{1-x}Sn_xPd_2$ enables simultaneous alterations to both the electronic structure and interatomic distances of the active site. By comparing $Ga_{1-x}Sn_xPd_2$, where both electronic and strain effects are significant, with $Ga_{1-x}In_xPd_2$, where electronic effects dominate and strain effects are minimal, the contributions of electronic structure and strain were disentangled. This comparison revealed that in $Ga_{1-x}Sn_xPd_2$, electronic effects dominate tin-rich compositions ($x \approx 0.93$), while strain effects are more pronounced in gallium-rich compositions ($x \approx 0.15$), resulting in two distinct high-activity regions for the methanol oxidation reaction (MOR). This method could potentially be applied to other intermetallic systems or reactions to differentiate the roles of electronic structure, geometric effects, and strain provided the systems are chosen carefully.[31−33]

Using Intermetallics to Create Strain Tuned Materials

Another method to evaluate strain in electrocatalysis involves the preparation of core−shell materials in which there is lattice mismatch between the core and the shell.[34,35] The change in the bond lengths brought about by strain causes the d-band center to shift which can weaken or strengthen the adsorption energy of reaction intermediates. Core−shell structures with solid solution cores are generally constrained to strain profiles that vary in only one direction, owing to a linear relationship between lattice constants and material composition (i.e., Vegard's law).[30] For instance, achieving compressive and tensile strains in Pt shells relative to elemental Pt necessitates the use of different elements—such as Ni for compressive strain and Au for tensile strain.[36] However, tuning strain by incorporating different elements into the core can introduce complications, as the shell—typically only a few atomic layers thick—may be susceptible to defects that expose the underlying core. The presence of these defects can trigger the bifunctional effect, particularly noticeable in reactions like the alkaline HOR, where the performance is drastically improved by presence of two elements on the surface.[37] This occurrence can obscure the changes in catalyst behavior from strain when comparing different catalyst systems. In contrast, the use of intermetallic

https://doi.org/10.1021/acsmaterialsau.4c00105
ACS Mater. Au 2025, 5, 231−238

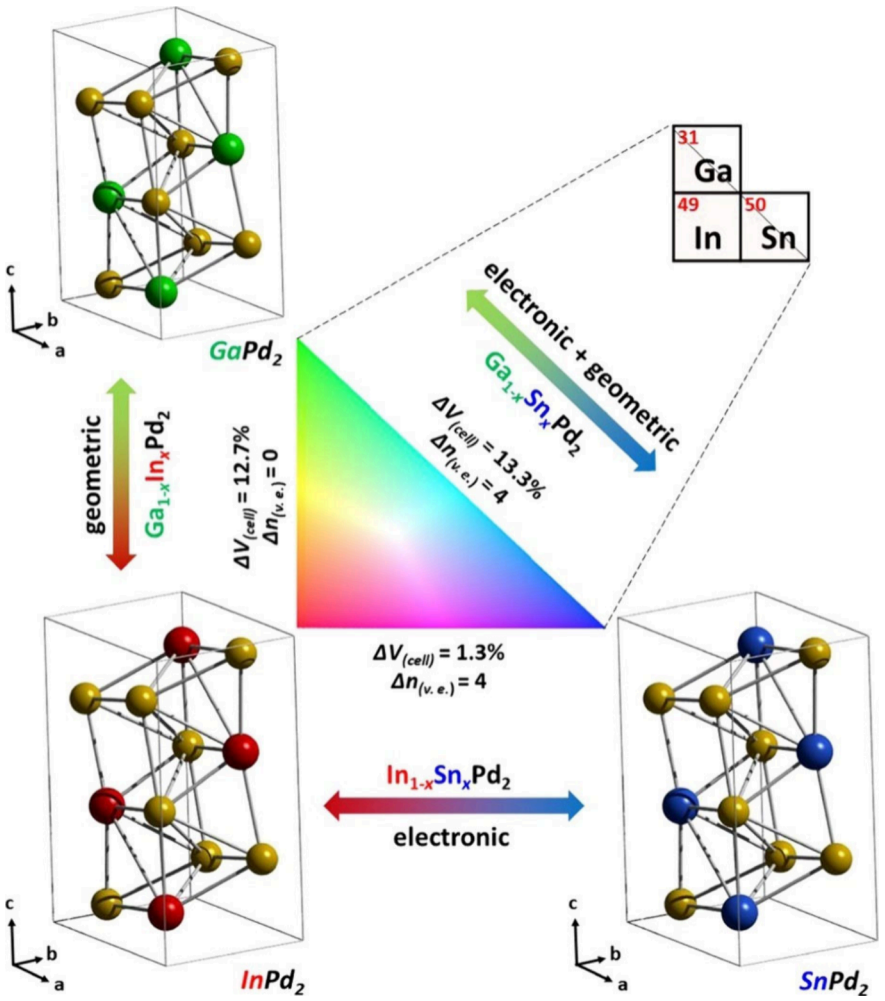


Figure 5. Isostructural compounds $GaPd_2$, $InPd_2$, and $SnPd_2$ with the controlled parameters within the ternary substitutional series. Figure reproduced from ref 31. Copyright 2022 American Chemical Society.

cores offers a distinct advantage: they enable the inclusion of both types of strains in a single binary alloy system.[38,39]

Intermetallic materials can be engineered to create strain profiles that are unattainable with conventional solid solution alloys. An interesting example was demonstrated in a study where Pt shells, grown over intermetallic PtPb nanoplates, exhibited significant biaxial strains.[39] The PtPb nanoplates are anisotropic, featuring two types of interfaces which impart different strain fields: {010}PtPb//{110}Pt at the edge of the plate, resulting in 7.5% tensile strain along the [01−1] direction and 1% compressive strain along the [110] direction (Figure 6a-b). At the top of the plate, the {001}PtPb//{110}Pt interface leads to the Pt shell being fully coherent to the PtPb core with 11% compressive strain along the [01−1]Pt and 7.5% tensile strain along [100]Pt (Figure 6a-b). This unique strain behavior is attributed to the long-range atomic ordering and change in the symmetry of crystal structure of the intermetallic PtPb core (relative to Pt), which promotes diverse strain profiles on the coherently formed Pt shells on its surface. These biaxially strained Pt materials demonstrated exceptional performance in the Oxygen Reduction Reaction (ORR), showing an 8-fold increase in reactivity compared to benchmark Pt catalysts (Figure 6c). This enhancement is due to the optimization of oxygen adsorption energy by altering the d-band center of the Pt surface.

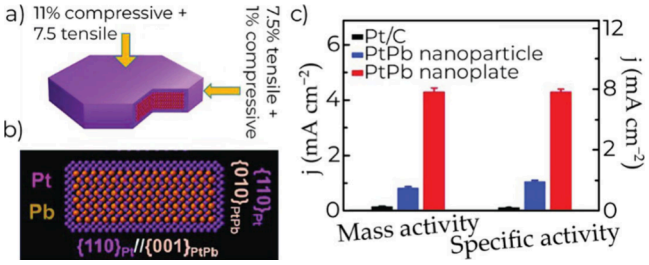


Figure 6. Schematic of PtPb nanoplate core with Pt shell a) showing the biaxial strain on the terrace and edge of the plate, b) Atomic-scale cross-sectional view, demonstrating the coherence between the Pt shell and the PtPb core. C) Oxygen reduction reaction (ORR) activity PtPb-Pt core−shell nanoplates with biaxial strain, PtPb-Pt core−shell nanoparticle that does not exhibit biaxial strain, and Pt/C benchmark catalyst. Figure adapted from ref 39. Copyright 2016 American Association for the Advancement of Science.

Another way to impart unique strain fields in core−shell architectures is to use materials composed of the same two elements but with varying crystal structures. In our recent study, we leveraged self-organized Pt shells on $PtSb_2$ (space group $Pa\bar{3}$) and PtSb (space group $P6_3/mmc$) to achieve architectures with tensile strain and compressive strain, respectively (Figure 7a-b).[38] This allowed us to modulate the hydrogen binding energy

https://doi.org/10.1021/acsmaterialsau.4c00105
ACS Mater. Au 2025, 5, 231−238

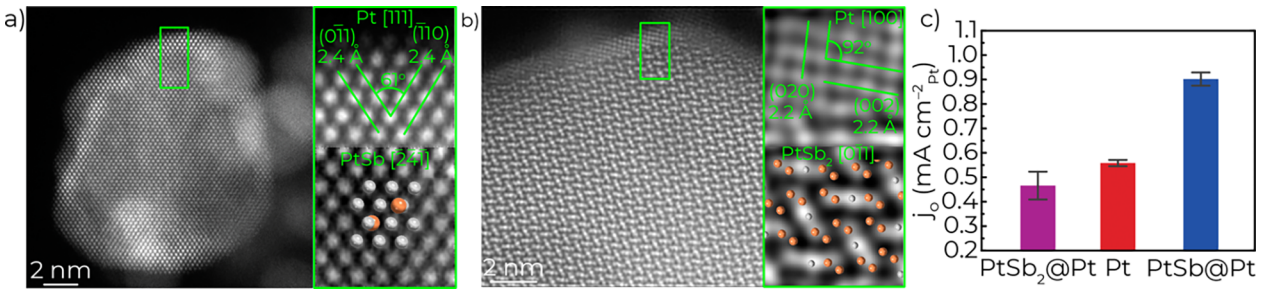


Figure 7. High-resolution scanning transmission electron microscopy (STEM) image of Pt−Sb intermetallic nanoparticles after cycling, showing: a) a PtSb@Pt structure with a compressively strained Pt shell, b) a $PtSb_2$@Pt structure with a tensile strained Pt shell. c) Comparison of mass-transport-corrected exchange current density (j_o), normalized by the electrochemically active surface area (ECSA), for Pt, PtSb@Pt, and $PtSb_2$@Pt, illustrating how strain influences the performance for the hydrogen oxidation reaction (HOR). Figure adapted from ref 38. Copyright 2023 American Chemical Society.

(HBE) on the Pt sites, enabling us to isolate the role of the HBE in the alkaline Hydrogen Oxidation Reaction (HOR). We revealed that compressively strained Pt, which lowers the HBE, exhibited 1.6 times greater activity compared to elemental Pt (Figure 7c). In contrast, tensile strained Pt, which increases the HBE, displayed activity approximately 20% lower than elemental Pt (Figure 7c). By using intermetallic cores with different crystal structures, we were able to incorporate both types of strain—compressive and tensile—within a single binary alloy system. This method avoids the need to introduce multiple alloying elements to achieve different strain fields, thereby circumventing complications related to bifunctional effects and providing a clearer understanding of how strain affects catalytic behavior. Although the role of the HBE as a key descriptor was previously debated, our study addresses this uncertainty, showing that the HBE is indeed critical for determining catalyst activity in alkaline HOR.[37,38,40,41]

Challenges and Opportunities in Intermetallic Catalyst Development

Although intermetallics possess well-defined atomic structures, maximizing their utility in fundamental studies requires materials that adopt morphologies exposing only a single surface termination (e.g., facet) at a time. In theory, single crystals would be ideal, providing a consistent, uniform surface for detailed analysis with various atomic-level characterization techniques. However, synthesizing intermetallic single crystals is challenging as many phases of interest do not congruently melt, which precludes the use of melting and solidification-based crystal growth approaches.[42,43] Furthermore, other complexities arise from the diverse physical properties of constituent metals, such as differing melting points and reactivity, which can lead to uneven compositions within the crystal.[42,43]

Given the complexities involved in synthesizing single-crystal intermetallics, one could turn to shape-controlled nanoparticles as an alternative.[24] The targeted growth of shape-controlled nanoparticles has been largely enabled by an extensive understanding of how structure-directing agents interact with material surfaces, facilitating the targeted expression of specific facets in systems like Au, Ag, Cu, Pt, and their solid-solution alloys.[24,44] Although shape-controlled intermetallic nanoparticles have been reported in the literature, most studies focus primarily on the performance of these nanoparticles in various applications, often lacking critical insights into how structure-directing agents control their growth. Consequently, we still lack a clear understanding of the design principles necessary for reliably producing intermetallic nanoparticles with controlled facet expression. While the synthesis of shape-controlled elemental and solid-solution alloy nanoparticles is not entirely perfected, there exists a substantial body of systematic work that the community can draw upon to rationally design these systems. As a result, current synthesis strategies for intermetallic nanoparticles often yield structures without controlled shapes, exposing multiple facets simultaneously. To bridge this gap, more fundamental studies on the growth mechanisms of intermetallic nanoparticles are essential.

Moreover, characterizing the surfaces of nanomaterials is inherently challenging, particularly when it comes to accurately identifying the facet distribution across the three-dimensional surface of nanoparticles. Conventional characterization techniques often lack the resolution or specificity needed for this level of detail, making it difficult to experimentally quantify facet-dependent reactivity. This complexity is exacerbated by the fact that the surface structure may differ from expectations due to surface reconstructions or compositional variations.[45,46] Additionally, studies have shown that nanomaterials may undergo structural changes during (electro)catalysis, adding further complexity to this task.[47−49] As characterization methods advance, the precise determination of the active site will become more accessible.[50,51] This advancement is crucial because, without precise control and understanding of surface structures, opportunities to fully optimize catalytic performance with intermetallics will remain challenging. Despite these challenges, the development of atomically well-defined materials holds the potential to revolutionize catalysis research, offering opportunities for designing more effective catalytic systems.

Overcoming these synthesis challenges is crucial because intermetallics offer the potential for precise control over active site geometries and electronic properties. This level of atomic precision enhances the predictability and reliability of catalytic properties, making intermetallics particularly suited for developing and training machine-learning models with clear, well-defined structures. For instance, initiatives like the Open Catalyst Project, CatBERTa, and others have modeled the adsorption energies of key reaction intermediates on specific intermetallic crystal facets to identify new materials with tailored catalytic functions.[52−55] However, without established methods to reliably produce intermetallics with the precise compositions and facets predicted, our ability to test these insights experimentally remains constrained, leaving a significant gap between predictions driven by artificial intelligence (AI) and real-world catalysts. To bridge this gap, computational approaches may play a more direct role in guiding the synthesis of shape-controlled intermetallic nanoparticles, enabling us to

https://doi.org/10.1021/acsmaterialsau.4c00105
ACS Mater. Au 2025, 5, 231−238

translate AI-driven predictions into experimentally realizable catalysts. AI-driven methods also offer opportunities beyond predicting new catalyst materials; they can assist in designing synthesis routes and predicting the most stable facets under specific synthesis conditions.

The atomic precision and structural order of intermetallics not only support the fine-tuning of catalyst properties but also help unlock deeper insights into the mechanisms underlying catalytic activity. Therefore, developing effective strategies for making shape-controlled intermetallic nanoparticles is pressing. Building a comprehensive understanding of intermetallic nanoparticle synthesis, akin to the advancements made for elemental and alloy nanoparticles in the early 2000s, will be essential. Such advancements would facilitate the transition to AI and machine-learning-driven approaches in catalysis, bridging the gap between computational predictions and experimental validation, and ultimately revolutionizing catalyst design.

CONCLUSION AND RECAP

The development of platforms that provide detailed insights into material structure and function is essential for advancing catalysis research. Intermetallics are particularly promising in this regard, as their atomically well-defined structures facilitate precise tuning of both active sites and the electronic structure of the material. Prioritizing the creation of well-defined materials—rather than solely aiming to produce high-performance catalysts through Edisonian methods—can significantly expand the boundaries of catalyst design. In fields like computational catalysis, these intermetallic materials are indispensable because they allow for the synthesis of systems that align better with computational models, thereby enhancing the correlation between experimental and theory. The study of intermetallic materials can facilitate the rational design of alloy catalysts, enabling the development of catalysts with predictable and adjustable behavior.

AUTHOR INFORMATION

Corresponding Author

Anthony Shoji Hall − *Department of Material Science and Engineering, Johns Hopkins University, Baltimore, Maryland 21218, United States;* Present Address: Department of Material Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States; orcid.org/0000-0003-4134-4160; Email: shoji@jhu.edu

Complete contact information is available at: https://pubs.acs.org/10.1021/acsmaterialsau.4c00105

Notes

The author declares no competing financial interest.

ACKNOWLEDGMENTS

A.S.H. acknowledges financial support from the National Science Foundation, under awards CBET-2326720, CHE-2102648 and DMR-2047019, and the American Chemical Society Petroleum Research Fund.

REFERENCES

(1) Lewis, N. S.; Nocera, D. G. Powering the planet: Chemical challenges in solar energy utilization. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103* (43), 15729−15735.

(2) Borup, R. L.; Kusoglu, A.; Neyerlin, K. C.; Mukundan, R.; Ahluwalia, R. K.; Cullen, D. A.; More, K. L.; Weber, A. Z.; Myers, D. J. Recent developments in catalyst-related PEM fuel cell durability. *Current Opinion in Electrochemistry* **2020**, *21*, 192−200.

(3) The Electrified Interface. In *Modern Electrochemistry 2A: Fundamentals of Electrodics*; Bockris, J. O. M., Reddy, A. K. N., Gamboa-Aldeco, M., Eds.; Springer US: Boston, MA, 2000; pp 771−1033.

(4) Sinfelt, J. H. *Bimetallic catalysts: discoveries, concepts, and applications*; Wiley: New York, 1983.

(5) Wang, D.; Xin, H. L.; Hovden, R.; Wang, H.; Yu, Y.; Muller, D. A.; DiSalvo, F. J.; Abruña, H. D. Structurally ordered intermetallic platinum−cobalt core−shell nanoparticles with enhanced activity and stability as oxygen reduction electrocatalysts. *Nat. Mater.* **2013**, *12* (1), 81−87.

(6) Stamenkovic, V. R.; Fowler, B.; Mun, B. S.; Wang, G.; Ross, P. N.; Lucas, C. A.; Marković, N. M. Improved Oxygen Reduction Activity on Pt3Ni (111) via Increased Surface Site Availability. *Science* **2007**, *315* (5811), 493−497.

(7) Koh, S.; Leisch, J.; Toney, M. F.; Strasser, P. Structure-Activity-Stability Relationships of Pt−Co Alloy Electrocatalysts in Gas-Diffusion Electrode Layers. *J. Phys. Chem. C* **2007**, *111* (9), 3744−3752.

(8) Becknell, N.; Son, Y.; Kim, D.; Li, D.; Yu, Y.; Niu, Z.; Lei, T.; Sneed, B. T.; More, K. L.; Markovic, N. M.; Stamenkovic, V. R.; Yang, P. Control of Architecture in Rhombic Dodecahedral Pt−Ni Nanoframe Electrocatalysts. *J. Am. Chem. Soc.* **2017**, *139* (34), 11678−11681.

(9) Serov, A.; Asset, T.; Padilla, M.; Matanovic, I.; Martinez, U.; Roy, A.; Artyushkova, K.; Chatenet, M.; Maillard, F.; Bayer, D.; Cremers, C.; Atanassov, P. Highly-active Pd−Cu electrocatalysts for oxidation of ubiquitous oxygenated fuels. *Applied Catalysis B: Environmental* **2016**, *191*, 76−85.

(10) Zhang, S.; Hao, Y.; Su, D.; Doan-Nguyen, V. V. T.; Wu, Y.; Li, J.; Sun, S.; Murray, C. B. Monodisperse Core/Shell Ni/FePt Nanoparticles and Their Conversion to Ni/Pt to Catalyze Oxygen Reduction. *J. Am. Chem. Soc.* **2014**, *136* (45), 15921−15924.

(11) Gamler, J. T. L.; Ashberry, H. M.; Skrabalak, S. E.; Koczkur, K. M. Random Alloyed versus Intermetallic Nanoparticles: A Comparison of Electrocatalytic Performance. *Adv. Mater.* **2018**, *30* (40), No. 1801563.

(12) Mutinda, S. I.; Li, D.; Kay, J.; Brock, S. L. Synthesis and characterization of Co2−xRhxP nanoparticles and their catalytic activity towards the oxygen evolution reaction. *Journal of Materials Chemistry A* **2018**, *6* (25), 12142−12152.

(13) Maroun, F.; Ozanam, F.; Magnussen, O. M.; Behm, R. J. The Role of Atomic Ensembles in the Reactivity of Bimetallic Electrocatalysts. *Science* **2001**, *293* (5536), 1811−1814.

(14) Li, H.; Shin, K.; Henkelman, G. Effects of ensembles, ligand, and strain on adsorbate binding to alloy surfaces. *J. Chem. Phys.* **2018**, *149* (17), No. 174705.

(15) Kim, C.; Dionigi, F.; Beermann, V.; Wang, X.; Möller, T.; Strasser, P. Alloy Nanocatalysts for the Electrochemical Oxygen Reduction (ORR) and the Direct Electrochemical Carbon Dioxide Reduction Reaction (CO2RR). *Adv. Mater.* **2019**, *31* (31), No. 1805617.

(16) Kim, D.; Resasco, J.; Yu, Y.; Asiri, A. M.; Yang, P. Synergistic geometric and electronic effects for electrochemical reduction of carbon dioxide using gold−copper bimetallic nanoparticles. *Nat. Commun.* **2014**, *5* (1), 4948.

(17) Tang, F.; Wang, L.; Dessie Walle, M.; Mustapha, A.; Liu, Y.-N. An alloy chemistry strategy to tailoring the d-band center of Ni by Cu for efficient and selective catalytic hydrogenation of furfural. *J. Catal.* **2020**, *383*, 172−180.

(18) Chen, B. W. J.; Xu, L.; Mavrikakis, M. Computational Methods in Heterogeneous Catalysis. *Chem. Rev.* **2021**, *121* (2), 1007−1048.

(19) Hammer, B.; Nørskov, J. K., Theoretical surface science and catalysis—calculations and concepts. *In Advances in Catalysis*; Academic Press: 2000; Vol. *45*, pp 71−129.

(20) Sachtler, W. M. H.; Van Der Plank, P. The role of individual surface atoms in chemisorption and catalysis by nickel-copper alloys. *Surf. Sci.* **1969**, *18* (1), 62−79.

(21) Ferrando, R.; Jellinek, J.; Johnston, R. L. Nanoalloys: From Theory to Applications of Alloy Clusters and Nanoparticles. *Chem. Rev.* **2008**, *108* (3), 845−910.
(22) Yang, X.; Hu, J.; Fu, J.; Wu, R.; Koel, B. E. Role of Surface Iron in Enhanced Activity for the Oxygen Reduction Reaction on a Pd3Fe(111) Single-Crystal Alloy. *Angew. Chem., Int. Ed.* **2011**, *50* (43), 10182−10185.
(23) Polak, M.; Rubinovich, L. The interplay of surface segregation and atomic order in alloys. *Surf. Sci. Rep.* **2000**, *38* (4), 127−194.
(24) Ruditskiy, A.; Peng, H.-C.; Xia, Y. Shape-Controlled Metal Nanocrystals for Heterogeneous Catalysis. *Annu. Rev. Chem. Biomol. Eng.* **2016**, *7*, 327−348.
(25) Meier, M.; Ledieu, J.; De Weerd, M. C.; Huang, Y.-T.; Abreu, G. J. P.; Pussi, K.; Diehl, R. D.; Mazet, T.; Fournée, V.; Gaudry, É. Interplay between bulk atomic clusters and surface structure in complex intermetallic compounds: The case study of the Al5Co2(001) surface. *Phys. Rev. B* **2015**, *91* (8), No. 085414.
(26) Bikondoa, O.; Castro, G. R.; Torrelles, X.; Wendler, F.; Moritz, W. Surface-induced disorder on the clean Ni3Al (111) surface. *Phys. Rev. B* **2005**, *72* (19), No. 195430.
(27) Kizilkaya, O.; Hite, D. A.; Zehner, D. M.; Sprunger, P. T. Surface reconstruction of FeAl(110) studied by scanning tunnelling microscopy and angle-resolved photoemission spectroscopy. *J. Phys.: Condens. Matter* **2004**, *16* (30), 5395.
(28) Ramesh, G. V.; Kodiyath, R.; Tanabe, T.; Manikandan, M.; Fujita, T.; Umezawa, N.; Ueda, S.; Ishihara, S.; Ariga, K.; Abe, H. Stimulation of Electro-oxidation Catalysis by Bulk-Structural Transformation in Intermetallic ZrPt3 Nanoparticles. *ACS Appl. Mater. Interfaces* **2014**, *6* (18), 16124−16130.
(29) Dasgupta, A.; He, H.; Gong, R.; Shang, S.-L.; Zimmerer, E. K.; Meyer, R. J.; Liu, Z.-K.; Janik, M. J.; Rioux, R. M. Atomic control of active-site ensembles in ordered alloys to enhance hydrogenation selectivity. *Nat. Chem.* **2022**, *14* (5), 523−529.
(30) Jacob, K. T.; Raj, S.; Rannesh, L. Vegard's law: a fundamental relation or an approximation? *International Journal of Materials Research* **2007**, *98* (9), 776−779.
(31) Zerdoumi, R.; Matselko, O.; Rößner, L.; Sarkar, B.; Grin, Y.; Armbrüster, M. Disentangling Electronic and Geometric Effects in Electrocatalysis through Substitution in Isostructural Intermetallic Compounds. *J. Am. Chem. Soc.* **2022**, *144* (18), 8379−8388.
(32) Zerdoumi, R.; Armbrüster, M. Insights into the Electronic Effects in Methanol Electro-Oxidation by Ternary In1−xSnxPd2 Intermetallic Compounds. *ACS Applied Energy Materials* **2021**, *4* (10), 11279−11289.
(33) Rößner, L.; Patiño Soriano, D. T.; Tiryaki, O.; Burkhardt, U.; Armbrüster, M. Synthesis of Isostructural Intermetallic Sn−Pb−Bi−Pt Platform Materials for Catalytic Investigations. *Inorg. Chem.* **2023**, *62* (11), 4688−4695.
(34) Strasser, P.; Koh, S.; Anniyev, T.; Greeley, J.; More, K.; Yu, C.; Liu, Z.; Kaya, S.; Nordlund, D.; Ogasawara, H.; Toney, M. F.; Nilsson, A. Lattice-strain control of the activity in dealloyed core−shell fuel cell catalysts. *Nat. Chem.* **2010**, *2* (6), 454−460.
(35) Moseley, P.; Curtin, W. A. Computational Design of Strain in Core−Shell Nanoparticles for Optimizing Catalytic Activity. *Nano Lett.* **2015**, *15* (6), 4089−4095.
(36) Hu, J.; Kuttiyiel, K. A.; Sasaki, K.; Zhang, C.; Adzic, R. R. Determination of Hydrogen Oxidation Reaction Mechanism Based on Pt−Had Energetics in Alkaline Electrolyte. *J. Electrochem. Soc.* **2018**, *165* (15), J3355.
(37) Li, J.; Ghoshal, S.; Bates, M. K.; Miller, T. E.; Davies, V.; Stavitski, E.; Attenkofer, K.; Mukerjee, S.; Ma, Z.-F.; Jia, Q. Experimental Proof of the Bifunctional Mechanism for the Hydrogen Oxidation in Alkaline Media. *Angew. Chem., Int. Ed.* **2017**, *56* (49), 15594−15598.
(38) Gong, T.; Alghamdi, H.; Raciti, D.; Hall, A. S. Improved Alkaline Hydrogen Oxidation on Strain-Modulated Pt Overlayers at Ordered Intermetallic Pt−Sb Cores. *ACS Energy Letters* **2023**, *8* (1), 685−690.
(39) Bu, L.; Zhang, N.; Guo, S.; Zhang, X.; Li, J.; Yao, J.; Wu, T.; Lu, G.; Ma, J.-Y.; Su, D.; Huang, X. Biaxially strained PtPb/Pt core/shell nanoplate boosts oxygen reduction catalysis. *Science* **2016**, *354* (6318), 1410−1414.
(40) Liao, Y.; Wang, S.; Zhang, Y.; Zhang, Y.; Gao, Y.; Mu, X.; Liu, S.; Wang, D.; Dai, Z. Advances in the study of HOR reaction mechanisms under alkaline conditions. *Advanced Sensor and Energy Materials* **2024**, *3* (1), No. 100089.
(41) Zheng, J.; Sheng, W.; Zhuang, Z.; Xu, B.; Yan, Y. Universal dependence of hydrogen oxidation and evolution reaction activity of platinum-group metals on pH and hydrogen binding energy. *Science Advances* **2016**, *2* (3), No. e1501602.
(42) Phelan, W. A.; Menard, M. C.; Kangas, M. J.; McCandless, G. T.; Drake, B. L.; Chan, J. Y. Adventures in Crystal Growth: Synthesis and Characterization of Single Crystals of Complex Intermetallic Compounds. *Chem. Mater.* **2012**, *24* (3), 409−420.
(43) Petrovic, C.; Canfield, P. C.; Mellen, J. Y. Growing intermetallic single crystals using in situ decanting. *Philos. Mag.* **2012**, *92* (19−21), 2448−2457.
(44) Gu, J.; Zhang, Y.-W.; Tao, F. Shape control of bimetallic nanocatalysts through well-designed colloidal chemistry approaches. *Chem. Soc. Rev.* **2012**, *41* (24), 8050−8065.
(45) Baer, D. R. Surface Characterization of Nanoparticles: critical needs and significant challenges. *Journal of Surface Analysis* **2011**, *17* (3), 163−169.
(46) Pan, B.; Chen, F.; Kou, B.; Wang, J.; Tang, Q.; Guo, L.; Wang, Q.; Li, Z.; Bian, W.; Wang, J. Unexpectedly high stability and surface reconstruction of PdAuAg nanoparticles for formate oxidation electrocatalysis. *Nanoscale* **2020**, *12* (21), 11659−11671.
(47) Yang, Y.; Louisia, S.; Yu, S.; Jin, J.; Roh, I.; Chen, C.; Fonseca Guzman, M. V.; Feijóo, J.; Chen, P.-C.; Wang, H.; Pollock, C. J.; Huang, X.; Shao, Y.-T.; Wang, C.; Muller, D. A.; Abruña, H. D.; Yang, P. Operando studies reveal active Cu nanograins for CO2 electroreduction. *Nature* **2023**, *614* (7947), 262−269.
(48) Grosse, P.; Yoon, A.; Rettenmaier, C.; Herzog, A.; Chee, S. W.; Roldan Cuenya, B. Dynamic transformation of cubic copper catalysts during CO2 electroreduction and its impact on catalytic selectivity. *Nat. Commun.* **2021**, *12* (1), 6736.
(49) Zhang, Q.; Song, Z.; Sun, X.; Liu, Y.; Wan, J.; Betzler, S. B.; Zheng, Q.; Shangguan, J.; Bustillo, K. C.; Ercius, P.; Narang, P.; Huang, Y.; Zheng, H. Atomic dynamics of electrified solid−liquid interfaces in liquid-cell TEM. *Nature* **2024**, *630* (8017), 643−647.
(50) Petkov, V.; Prasai, B.; Shastri, S.; Kim, J.-W.; Shan, S.; Kareem, H. R.; Luo, J.; Zhong, C.-J. Surface Atomic Structure and Functionality of Metallic Nanoparticles: A Case Study of Au−Pd Nanoalloy Catalysts. *J. Phys. Chem. C* **2017**, *121* (14), 7854−7866.
(51) Lee, J.; Jeong, C.; Yang, Y. Single-atom level determination of 3-dimensional surface atomic structure via neural network-assisted atomic electron tomography. *Nat. Commun.* **2021**, *12* (1), 1962.
(52) Li, Z.; Wang, S.; Xin, H. Toward artificial intelligence in catalysis. *Nature Catalysis* **2018**, *1* (9), 641−642.
(53) Tran, K.; Ulissi, Z. W. Active Learning Across Intermetallics to Guide Discovery of Electrocatalysts for CO2 Reduction and H2 Evolution. *Nat Catal.* **2018**, *1*, 696−703.
(54) Ock, J.; Guntuboina, C.; Barati Farimani, A. Catalyst Energy Prediction with CatBERTa: Unveiling Feature Exploration Strategies through Large Language Models. *ACS Catal.* **2023**, *13* (24), 16032−16044.
(55) Korovin, A. N.; Humonen, I. S.; Samtsevich, A. I.; Eremin, R. A.; Vasilev, A. I.; Lazarev, V. D.; Budennyy, S. A. Boosting heterogeneous catalyst discovery by structurally constrained deep learning models. *Materials Today Chemistry* **2023**, *30*, No. 101541.

https://doi.org/10.1021/acsmaterialsau.4c00105
ACS Mater. Au 2025, 5, 231−238