

Design Principles for Multinary Metal Chalcogenides: Toward Programmable Reactivity in Energy Conversion[†]

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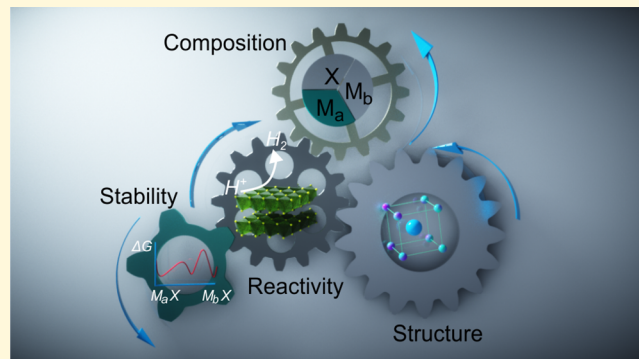
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ABSTRACT: Transformative solutions to contemporary energy problems hinge on the successful development of non-noble functional materials. A promising avenue toward sustainable energy conversion and storage is the synthesis and integration of electrocatalyst materials with interfaces that drive small-molecule electroreduction reactions like CO₂ and CO conversion to fuels, as well as hydrogen production from water. While research advances in the past several decades have led to deployable technologies on both of these fronts, industrial scalability is undercut by high material cost, lack of catalyst selectivity, and poor long-term operational stability. In this perspective, we highlight the exceptional promise of multinary chalcogenides as an expansive yet underexplored composition space where catalytic functionality and synthesizability can be predicted and finely controlled by leveraging nominal composition, dimensionality, crystallinity, and morphology. We further outline a path forward for chalcogenide material discovery that integrates theory with experiment to rationally inform material design and accelerate the synthesis of functional energy materials.



1. INTRODUCTION

The demand for advanced functional materials is constantly evolving to meet the contemporary needs of industrial, commercial, and personal consumers. As a pressing example, technologies like energy conversion and storage are rapidly accelerating in their sophistication as a result of increasing global energy consumption and presently heavy reliance on combustion of fossil fuel derivatives. Transitioning to promising renewable energy sources like wind and solar as our predominant strategy for meeting growing energy demands in a carbon negative or carbon neutral way is, unfortunately, impeded by the intermittent nature of both power sources. This in turn motivates the development of energy conversion and storage materials that can mediate the transformation of transient electrical energy into chemically stable fossil fuel analogues,^{1,2} hydrogen gas,^{3,4} or potential energy via battery architectures.^{5,6} To achieve any of these promising modalities, we must design and implement functional materials that drive specific physicochemical processes—ranging from small molecule electrocatalysis in the case of converting electrical energy directly to fuels, all the way to charged species uptake within the interstitial sites of a solid structure in the case of rechargeable batteries.

In the specific example of solar-to-fuels technology, materials must be designed that convert solar electricity directly to fuels

(photoelectrochemical processes)^{7,8} or that convert solar-sourced electricity to fuels in tandem photovoltaic—electrolyzer (PV-electrolyzer, Figure 1) constructs.^{9–11} Material performance considerations associated with either task are plentiful; perhaps most importantly, functional material compositions are ones that effectively reduce energy penalties for the desired chemical conversion process. A good example of where this is required is the hydrogen evolution reaction (HER) that has the balanced half reaction shown in eq 1:



An unfortunate reality is that the most efficient (i.e., low energy penalties and high rates of fuel production) catalytic mediations of reactions like the HER have required non-abundant elements like Pt, Ru, and Ir that engender prohibitively expensive material costs for their large-scale deployment.^{3,12,13} An increasingly popular strategy for mitigating this composition-based limitation is the design of entirely Earth-abundant materials that also mediate desirable

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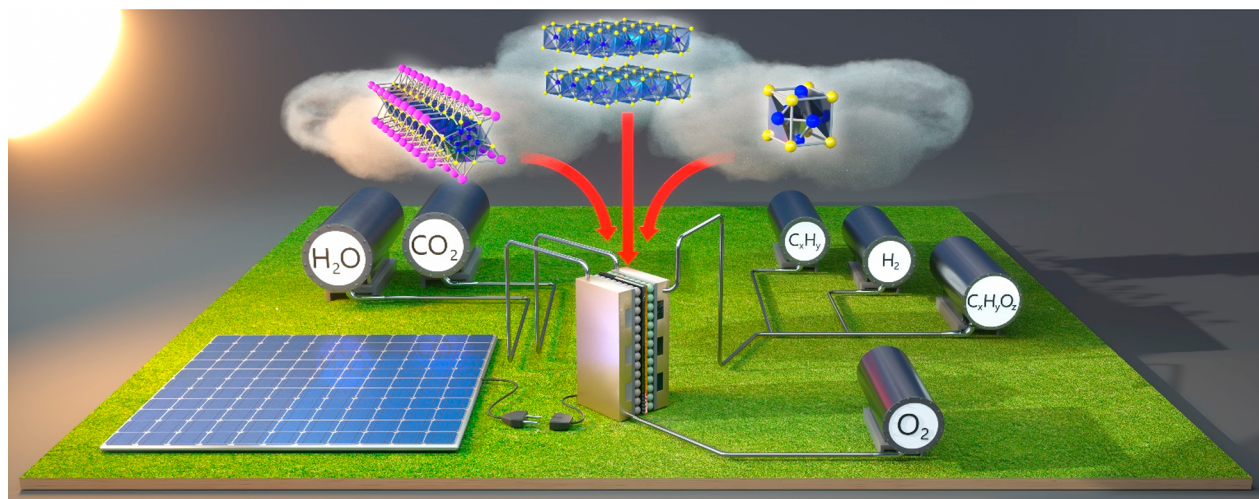


Figure 1. Illustration of a PV-electrolyzer architecture wherein water and recycled or captured CO₂ are electro-reduced to value-added products using solar electricity as a driving force. In this work, we focus specifically on 0D–3D chalcogenide frameworks as shown here that also have tunable reactivity and stability and can be integrated into such a system to facilitate contemporarily relevant chemical reactions.

energy conversion reactions such as the aforementioned HER (to generate hydrogen gas for combustion or for use in fuel cells),^{14–16} the CO₂ reduction (CO₂R) reaction (to form oxygenates and hydrocarbon fuels),^{17,18} oxygen evolution reaction (OER) (to balance cathodic reactions like HER and CO₂R),^{19,20} oxygen reduction reaction (ORR) (for fuel cell applications and peroxide synthesis),^{21–23} and nitrogen reduction reaction (N₂R) (for fixing N₂ as NH₃).²⁴ In expanding our search for catalytically reactive materials to multinary extended solids, we introduce a broad landscape of physicochemical properties like oxophilicity, conductivity, and thermodynamic stability that all change as the composition, structure, and dimensionality of materials change. This flexibility complicates the search for viable material spaces that can help address our energy needs. This is because interwoven into each composition-driven improvement in one reactivity metric (e.g., reduced charge-transfer resistance for an electrochemical conversion reaction) can be a series of other—sometimes detrimental in their nature—changes in reactivity metrics. Hence in this work we highlight efforts by chalcogenide researchers to construct meaningful structure–function relationships that are based upon the beneficial tuning of singular physicochemical properties for reactions of interest. An important caveat that lies at the crux of contemporary materials design is that as a composition approaches “ideality” in a given metric, it may deviate from “ideality” in another. As a result of this ubiquitous dichotomy, our use of terms such as “ideal” and “optimal” are inherently subjective and serve to highlight improvements to the property of interest—be it adsorption affinity, morphology, or even thermodynamic stability. We suggest that the concept of optimality for multinary compositions of interest for energy applications should be tied to their economic viability. In other words, it is the aggregate of reactivity, stability, and scalability that dictates the optimality of a material. For our purposes here, the critical consideration is that despite this system-dependent definition of ideality, multinary chalcogenides enable near-infinite control with which researchers can leverage the very same composition-dependent variables (crystallinity, dimensionality, electronic structure, etc.) that simultaneously complicate our search for viable materials. Hence we must be diligent in our

extraction of meaningful properties that allow for the construction of informative composition–structure–function relationships.

In the example of energy storage via charged ion intercalation/deintercalation, host materials must be designed that meet a swath of requirements in order to enable stable, high-capacity cycling behavior. To mediate monovalent Li⁺, divalent Mg²⁺, or even trivalent Al³⁺ ion intercalation, cathode materials must be stable in fairly harsh organic electrolytes and under external applied potentials, as well as over the course of repeated insertion and removal of ions from interstitial sites within their structure. In addition to this functional stability, cathodes must support high gravimetric and volumetric energy densities which is theoretically achievable for structures with an appreciable affinity for hosting multivalent species. However, this affinity comes with the added cost of lower intercalant mobility and cycling stability due to increased electrostatic penalties that render migration kinetics sluggish. Circumventing this ubiquitous kinetic limitation for multivalent battery cathodes has been successful when using chalcogenide-based frameworks such as the Chevrel phase (CP) M_yMo₆X₈ (M = alkali, alkaline, transition, post-transition metal; y = 0–4; X = S, Se, Te) and thiospinel AB₂S₄ (A = Li, Cu; B = first-row transition metal) frameworks. Unfortunately, these flexible composition spaces suffer from low discharge voltages,^{25–27} motivating further optimization of the interstitial chemistry that dictates their power output as battery materials. Despite the apparent drawbacks of chalcogenide-based cathode materials, their initial promise as multivalent cathodes stems largely from their compositional and structural flexibility. That flexibility underpins many of the insights discussed in this perspective as they relate to the design of new energy materials comprised of S-, Se-, and Te-based extended solids.

The expansive metal-chalcogenide composition space has profound promise in energy conversion applications like electrocatalysis and photoelectrocatalysis, as the functionality, stability, low cost, and even large-scale processability of chalcogenides can be controlled via careful selection and arrangement of their constituent elements. In this perspective, we illustrate some of the promising functionality that has been observed for pseudomolecular and dimensionally controlled

multinary chalcogenides, and we further outline the foundations of design strategies for chalcogenide-based frameworks that have applications in energy conversion technologies like electro- and photoelectrocatalysis. Said strategies will necessarily leverage the synthetic flexibility, catalytic reactivity, and functional stability of metal chalcogenides, as discussed herein.

Integrated experimental and computational approaches to chalcogenide design have already been established in some areas, and we expect that future developments in functionality for these highly compositional tunable materials (Figure 2) will

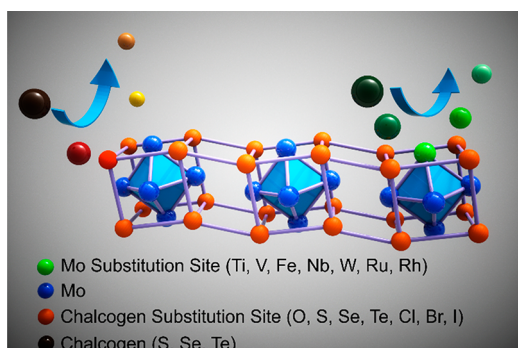


Figure 2. Illustration of the compositional flexibility afforded by the pseudo-molecular Chevrel phase Mo_6X_8 structure type wherein chalcogen sites (red/orange) and molybdenum sites (blue/green) are interchangeable via solid-state synthetic chemistry.

be necessarily borne out of evolving synergistic efforts by experimentalists and theoreticians. It should be noted that while this perspective focuses specifically on energy conversion applications, these broad material families have applications in nanoelectronics,^{28–31} multivalent batteries,^{5,6} thermal catalysts,^{32–35} semiconductors,^{36–38} protective coatings,^{39–42}

lubricants,^{43–45} and a host of other applications that serve to benefit from advanced materials design strategies.

2. SYNTHETIC FLEXIBILITY

Advancing the state-of-the-art in materials design principles for pseudo-molecular and dimensionally controlled chalcogenides has been an expanding effort for the past decade.^{46–48} The vast *compositional* flexibility of these multinary systems yields a seemingly comparable *structural* flexibility—thereby enabling, for example, the synthesis of multiple unique polymorphs for the same nominal compositions,^{49–51} as well as the synthesis of multiple unique crystal structures depending on the metal-to-chalcogen ratio⁵² and synthetic conditions like temperature⁵³ and pressure.⁵⁴

2.1. Surface Energy Effects on Anisotropic Growth.

For any given multinary chalcogenide system (e.g., $\text{M}_a\text{M}_b\text{X}$), changing the nominal target composition of a structure based on the precursor selection will tend to favor specific crystallographic configurations. These configurations depend on a thermodynamic stability that is largely determined by bond enthalpies of the target product phase relative to bond enthalpies of the competing decomposition product phases, as well as on the entropy of target phases (particularly those that are synthesized at high temperatures).⁵⁵ Additionally, these configurations depend on the growth kinetics of the target product phase which are driven by precursor processing conditions and reaction temperatures, as well as anisotropy in growth facet stabilization. For example, chalcogen-deficient Mo-based phases having the stoichiometry $\text{M}_2\text{Mo}_6\text{S}_6$ tend to nucleate strongly along one dimension (see Figure 3) owing to sufficiently strong Mo–Mo and Mo–S bonding and incredibly low surface energies for facets parallel to the hexagonal growth axis.³⁰ In contrast, chalcogen-rich MX_2 's (e.g., $\text{M} = \text{Mo}$ and W and $\text{X} = \text{S}$, Se , and Te) grow conspicuously in two dimensions owing to their stacked VdW-layered crystal structures that exhibit a thermodynamic preference for monolayer config-

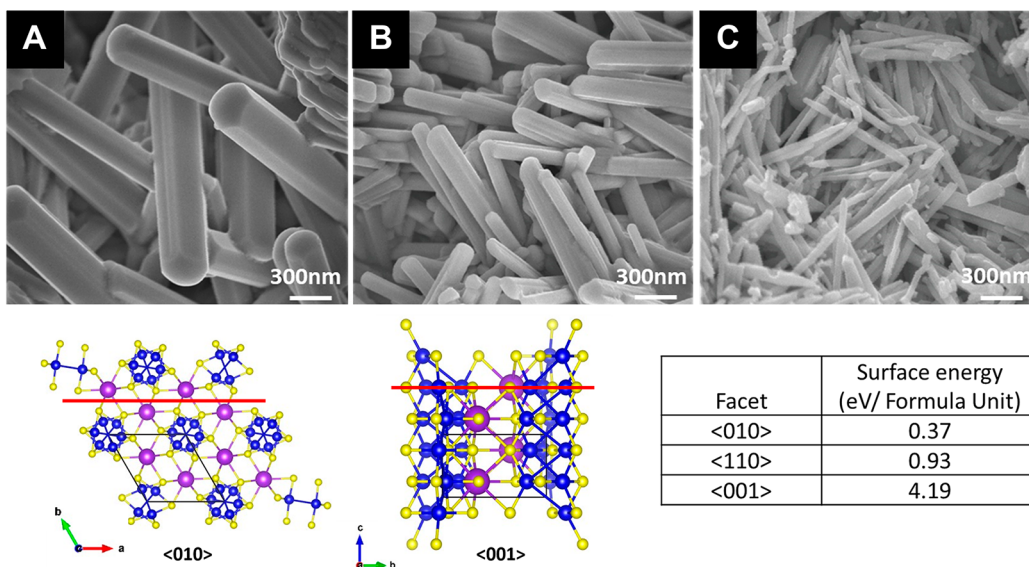


Figure 3. Evidence of structure-driven anisotropic growth of chalcogenide nanomaterials in the $\text{M}_2\text{Mo}_6\text{S}_6$ pseudo-Chevrel phase family, including SEM images of (A) $\text{K}_2\text{Mo}_6\text{S}_6$ nanorods, (B) $\text{Rb}_2\text{Mo}_6\text{S}_6$ nanorods, and (C) $\text{Cs}_2\text{Mo}_6\text{S}_6$ nanorods, alongside crystal structure representations illustrating <010> and <001> directions with their respective surface free energies. In this hexagonal structure the strong preferential formation of the <010> surface is sufficient in directing one-dimensional nucleation in a surfactant-free solid-state reaction. Copyright 2020 Royal Society of Chemistry. Figure reproduced with permission from ref 30.

urations at small-area coverages and multilayer preference at large-area coverage.⁵⁶

2.2. Synthetic Methods for Achieving Dimensional Control. The complex nature of the interplay between dimensionality and electrocatalytic reactivity in dimensionally controlled chalcogenides remains to be fully unraveled. However, there are many examples of solid-state,^{57,58} hydrothermal/solvothermal,^{59,60} chemical vapor deposition,^{61–63} ionic liquid,⁶⁴ and surfactant-assisted^{65,66} methodologies for synthesizing dimensionally and compositionally controlled chalcogenide structures. Zhang et al. synthesized the entire range of 0D–3D structures based on thioarsenate motifs in their work where polyvinylpyrrolidone, polyethylene glycol-400, and 1-hexadecyl-3-methylimidazolium chloride were used as surfactants to generate 0D $[\text{NH}_4]_8[\text{Mn}_2\text{As}_4\text{S}_{16}]$, 1D $[\text{Mn}(\text{NH}_3)_6][\text{Mn}_2\text{As}_2\text{S}_8(\text{N}_2\text{H}_4)]$, 2D $[\text{enH}][\text{Cu}_3\text{As}_2\text{S}_5]$, and 3D $[\text{NH}_4][\text{MnAs}_3\text{S}_6]$.⁶⁷ Additional studies involving surfactants for the synthesis of chalcogenide materials extended this methodology to other new 2D selenidostannates,⁶⁸ oxosulfides,⁶⁹ chalcogenidogermanates,⁷⁰ and numerous others.^{65,66} The successful linking of chalcogenide motifs through surfactant chemistry is a very promising route toward novel composites having dimensionality-directed physicochemical properties, and may therefore offer a low-cost and scalable alternative to existing solid-state synthetic methods.

Another effective method in generating 0D–3D structures is by manipulating the composition of binary parent structures. Work by Kanatzidis et al. highlights the phenomenon wherein 3D binary host lattices (e.g., HgX ; $\text{X} = \text{S}, \text{Se}, \text{Te}$) can be dimensionally reduced upon introduction of another binary composition A_2X ($\text{A} = \text{alkali}$; $\text{X} = \text{S}, \text{Se}, \text{Te}$).⁷¹ This introduction implants X^{2-} species into the parent lattice to form anionic $[\text{M}_x\text{X}_y]^{n-}$ frameworks at varying levels of lower dimensionality, with A^+ acting as a charge-balancing spacer between the anionic metal chalcogenide domains. Because increasing A_2X content requires additional accommodation of X^{2-} by the parent compound, the continuity of the 3D parent structure is diminished to form lower dimensional analogues (Figure 4). Importantly, this route affords a level of control over the band structure of the resulting materials, as the 3D parent structures tend to exhibit strong orbital overlap by the nature of their connectivity, although disruption of this bonding continuity upon incorporation of A_2X reduces the orbital overlap—thereby yielding narrower bands and effectively widening the band gap.

Promising recent work by Schaak et al. also highlights the precise synthetic tunability afforded by nanoparticulate chalcogenide synthesis.⁷² For example, in a recent work from their group it was shown that controlling cation exchange in metal sulfide nanoparticles enabled a low-temperature alternative to traditional high-temperature routes toward high-entropy materials.⁷³ In this work, colloidal nanoparticles including $\text{Zn}/\text{Co}/\text{Cu}/\text{In}/\text{Ga}$ in a $\text{Cu}_{1.8}\text{S}$ parent structure were synthesized for the first time by leveraging thermodynamics of cation solvation and configurational enthalpy. In a related work, Schaak et al. demonstrated the effective generation of ZnS nanocrystals with modular stacking fault density (Figure 5) that was controllable by affecting the cation exchange rate, which was found to depend largely on reagent concentration and temperature for the $\text{Cu}_{1.8}\text{S} \rightarrow \text{ZnS}$ system that was studied.⁷⁴

With the goal of mitigating intensive time and energy inputs that are traditionally required to achieve solid-state synthesis of

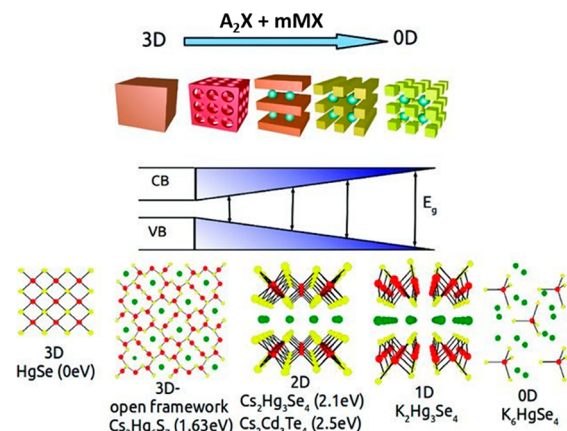


Figure 4. Outline of the progression of dimensionalities achievable in metal chalcogenides. Alkali metals are depicted as the green spheres, metal elements are shown as the red spheres, and chalcogen elements are shown as yellow spheres. Typical examples shown include: $\text{Cs}_2\text{Hg}_3\text{S}_7$, an open-framework 3D tetragonal structure; $\text{Cs}_2\text{Hg}_3\text{Se}_4$ and $\text{Cs}_2\text{Cd}_3\text{Te}_4$, 2D layered compounds; $\text{K}_2\text{Hg}_3\text{Se}_4$, a compound that exhibits quasi-1D Hg–Se chains (here depicted along the b axis); and K_6HgSe_4 , in which the increased Se/Hg ratio forces the dimensionality to 0, i.e., the appearance of isolated Hg–Se pyramidal structures (molecular salt). The above structures exhibit a blue shift in their bandgap with respect to the metal binary basis. Copyright 2011 John Wiley & Sons. Figure reproduced with permission.⁷¹

high-temperature chalcogenide phases, our group has recently expanded upon susceptor-enhanced microwave irradiation protocols^{75,76} wherein conventional microwave irradiation can encourage reactor temperatures as high as 1200 °C and pure-phase chalcogenide formation in 5–10 min. This protocol has proven effective in accelerating the synthesis of an array of binary and ternary Chevrel phases (CPs) in the sulfide, selenide, and telluride composition spaces,^{77–79} as well as sulfide, selenide and telluride pseudo-Chevrel phases (PCPs) intercalated by K, Rb, and Cs.³⁰ This robust solid-state microwave synthesis methodology is yet another testament to the compositional flexibility one can leverage to establish extensive chalcogenide libraries over which functionality can ultimately be explored. However, many emerging avenues toward growth of dimensionally and morphologically controlled multinary chalcogenides remain to be explored, including phototropic growth,⁸⁰ electrodeposition,^{81,82} and even in situ microscopy-driven top-down synthesis.^{83,84} Specifically, we review here several instances of synthetically accessible, compositionally and dimensionally controllable metal chalcogenides performing catalytic small-molecule conversion reactions, with the goal of highlighting the role of morphology and composition in each case.

3. CATALYTIC REACTIVITY

Metal chalcogenides have long been touted for their ability to mediate electrocatalytic conversion reactions like HER, CO_2R , COR, OER, and ORR, largely owing to the immense landscape of compositions having amenable electronic structures, as well as well-defined multinary active sites. From edge-sites of two-dimensional MoS_2 which rival Pt in HER electrocatalysis,⁸⁵ to its vacancy-rich basal planes which exhibit C–C coupling reactivity for the generation of products beyond CO, formate, and methanol (e.g., n -propanol),^{86,87} to isolated square planar Mo–S coordination in Chevrel phase Mo_6S_8 that encourages

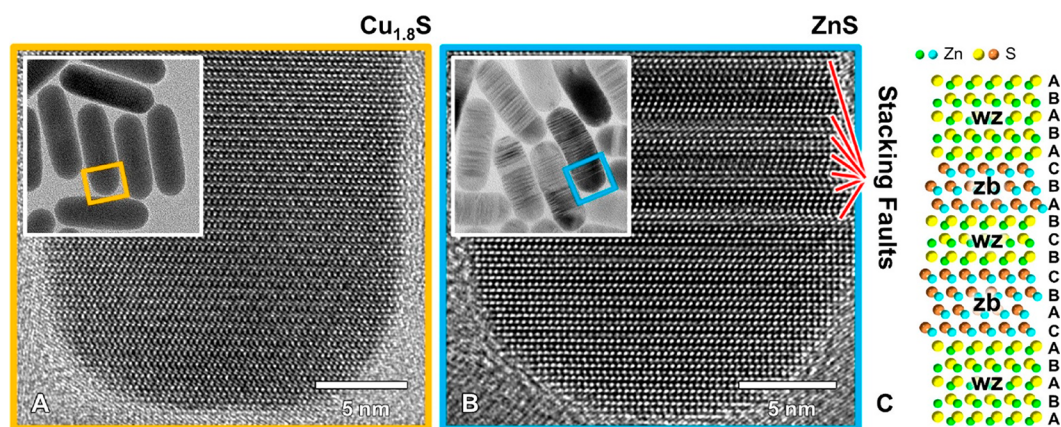


Figure 5. (A, B) TEM and HRTEM images of (A) $\text{Cu}_{1.8}\text{S}$ precursor and (B) ZnS product nanorods. (C) Crystallographic model of stacking faults resulting from hcp wurtzite (wz) layers transitioning to ccp zincblende (zb). Copyright 2021 American Chemical Society. Figure reproduced with permission.⁷³

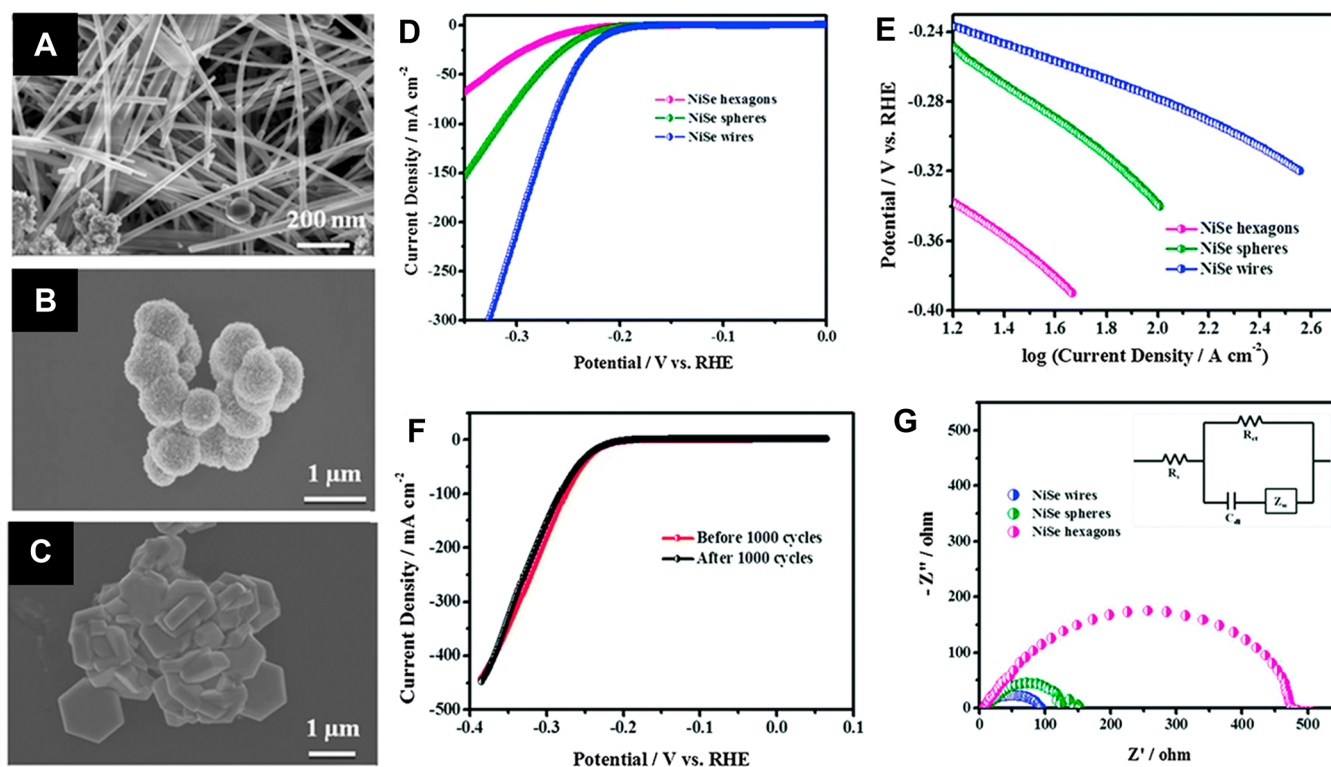


Figure 6. (A–C) SEM images illustrating the morphology of NiSe (A) wires, (B) spheres, and (C) plates. (D) Linear polarization curves obtained with different morphologies of NiSe and (E) corresponding Tafel plots for a catalyst loading of 0.56 mg/cm^2 . (F) Linear sweep voltammograms for the NiSe nanowire catalyst (before and after 1000 cycles). (G) Electrochemical impedance spectra of wires, spheres, and hexagons obtained with an AC amplitude of 5 mV at a DC bias of -0.235 V (inset gives the equivalent circuit used). Copyright 2015 Royal Society of Chemistry. Figure reproduced with permission.⁸⁹

selective reduction to methanol⁷⁹—an immense landscape of energy materials remains to be discovered through targeted engineering of surface structure and active site composition.

3.1. Morphology and Crystallinity Effects on Reactivity. The arrangement of chalcogenides into unique but well-defined crystal structures and morphologies within a singular composition can be controlled by careful selection of precursors and reaction conditions. Indeed, these processing conditions can introduce a pronounced effect on electrocatalytic reactivity.⁸⁸ Work by Sampath et al.⁸⁹ (Figure 6) on nickel selenide (NiSe) highlights the importance of synthesizing “ideal” chalcogenide morphologies for improving catalytic

reactivity: in this work, wire-like, sphere-like, and plate-like selenides having the same hexagonal crystal structure were analyzed as HER, ORR, and glucose oxidation catalysts. It was found the overpotentials required to achieve a normalized HER current density of -50 mA/cm^2 (Figure 6d) were -0.26 V , -0.30 V , and -0.40 V for wires, spheres, and plates, respectively. This indicates that the increase in catalytic performance is attributable to surface structure differences as well as the predominance of specific reactive crystallographic planes, rather than simply to an increase in surface area which is often posited as the culprit when discussing morphology studies. This facet-dependence phenomenon has been well-

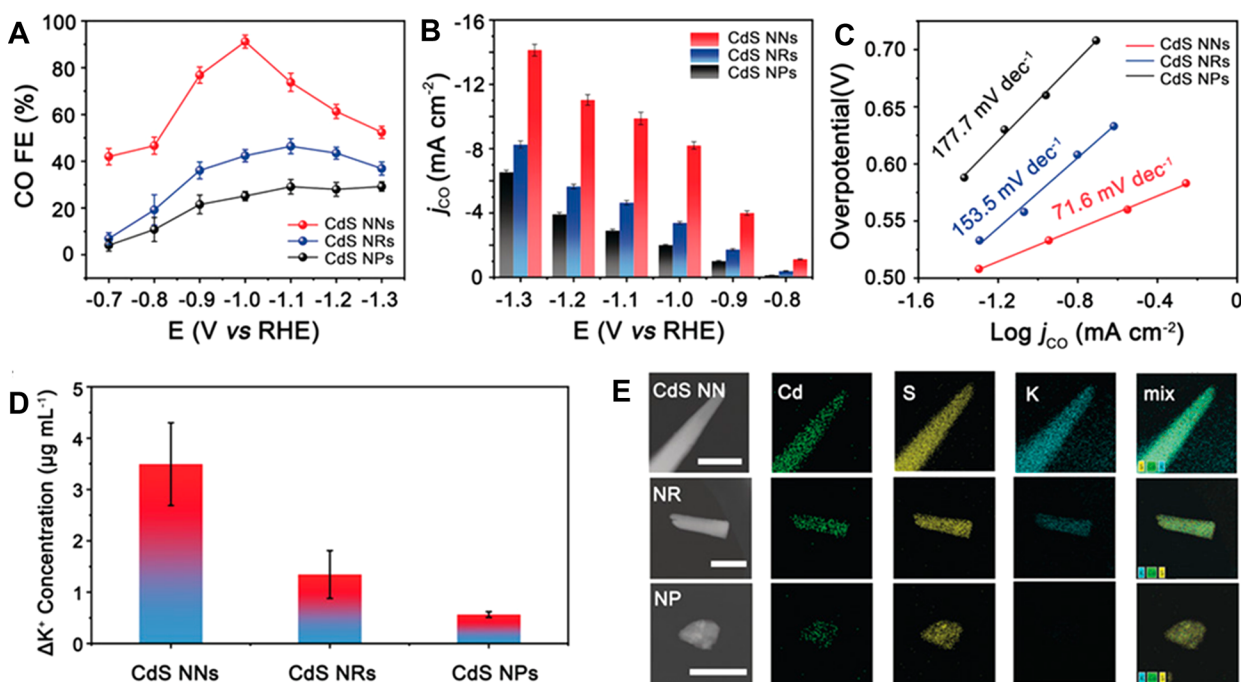


Figure 7. CO₂RR performances on CdS needles, rods, and particles in an H-cell system. (A) CO Faradaic efficiencies for CdS needles, rods, and particles at varying applied potentials. (B) Current densities for CO production at varying applied potentials on CdS needles, rods, and particles. (C) CO₂ Tafel analysis of the CdS needles, rods, and particles. (D) Field-induced K⁺ concentration loss in the electrolytes caused by CdS needles, rods, and particles. (E) Elemental mapping of CdS needles, rods, and particles that ran in 0.1 M KHCO₃ at -1.0 V vs RHE for 5 min, showing enhanced K⁺ concentration on high-curvature CdS needles. Scale bars: 250 nm. Copyright 1999–2021 John Wiley & Sons, Inc. Figure reproduced with permission.⁹⁸

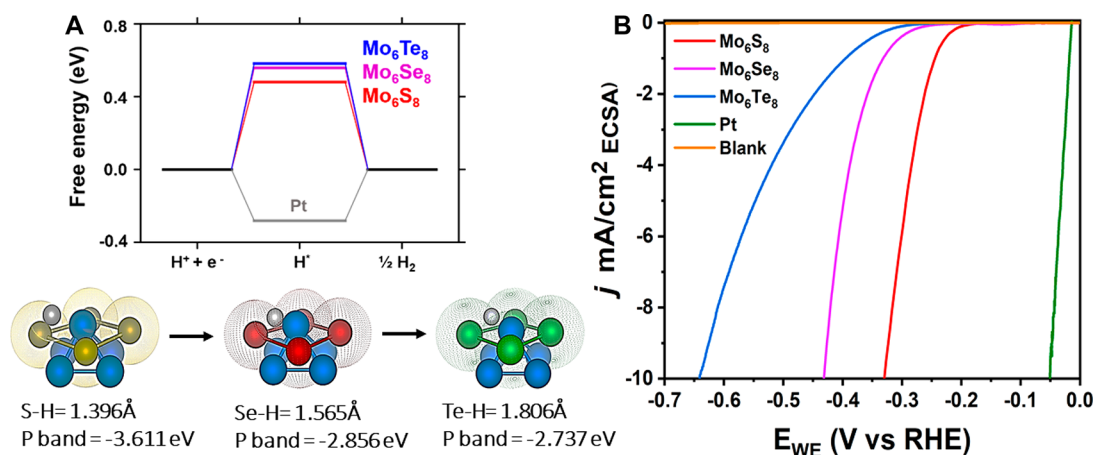


Figure 8. (A) Calculated adsorption energies of H* (ΔG_H) on all three binary Mo₆X₈ compositions compared to Pt along with the calculated X–H distances and p band positions over each CP investigated in the study. Local contribution of Mo₆X₈ structure is approximated by the X–H bond length that scales directly with DFT ΔG_H and HER overpotentials while the bulk electronic structure contribution is approximated by the p band center position that scales inversely with observed HER overpotentials. (B) HER polarization curves for CP chalcogenide electrodes in 0.5 M H₂SO₄, along with 20% Pt/C on Vulcan Carbon Cloth and a blank (carbon paper with PTFE/carbon black/IPA ink) for comparison. Copyright 2020 American Chemical Society. Figure reproduced with permission from ref 78.

studied in metal^{90,91} and metal-oxide^{92,93} catalysts but remains underexplored for chalcogenide electrocatalysts. To this end, work by Vrubel et al.,⁹⁴ Cao et al.,⁹⁵ and Wu et al.⁹⁶ explore the origin of improved catalytic HER activity in amorphous MoS₂ (a-MoS_x) in comparison to its crystalline analogue (c-MoS₂). This activity arises largely from the improved adsorption energetics at under-coordinated Mo and S sites in a-MoS₂, as well as persistently contracted Mo–Mo bonds in a-MoS_x that—while similar in structure to Mo-terminated edges of highly active 1T MoS₂—persist under electrochemical

reduction (unlike for 1T MoS₂). On a related note, the existence of multiple stable polymorphs in MX₂'s allows for additional comparisons across compositions such as MoS₂ wherein one polymorph—the semiconducting 2H phase—exhibits impressive edge-site reactivity for HER⁸⁵ that actually increases for the metallic 1T phase owing to the improved electrical conductivity of the edges that facilitates charge-transfer kinetics relative to the semiconducting 2H phase.^{96,97}

In addition to surface faceting and polymorph control as a means of directing reactivity toward specific products, catalyst

morphology has been shown to play a significant role in improving performance (Figure 7). Gao et al.⁹⁸ showed that morphology effects alone accounted for electric field enhancement that led to a CO₂-to-CO conversion efficiency (Figure 7a) of 91.1% at −1.0 V vs RHE over needle-like CdS, compared to analogous rod-like (42.4%) and nanoparticulate (25.1%) CdS where relative surface curvature was minimal and resulting tip-enhancement of the interfacial electric field was reduced.

These observable improvements to catalytic reactivity provide strong motivation for the careful selection of synthetic methodologies where reactivity-directing material properties like morphology and crystallinity can be truly optimized. However, the intrinsic reactivity of these aforementioned catalytic systems also depends strongly on the multinary composition of their catalytically active sites. Hence, we must develop our understanding of how composition changes can affect reactivity.

3.2. Composition Effects on Reactivity. Metal chalcogenides are renowned for their compositional flexibility. Their ability to retain specific structure types over broad ranges of metal and chalcogen compositions has made them excellent model systems for exploring composition effects on catalytic reactivity. This is true regardless of whether those effects arise from modulated electrical conductivity, band structure or band positions, charge density, or some combination thereof. To date, no chalcogenide family has been systematically evaluated as electrocatalysts for HER to a greater extent than the dichalcogenide MX₂'s (M = Group IV, Group V, Group VI, and Group VII; X = S, Se, Te), with much emphasis having been placed on the design principle that basal plane and edge conductivities are critical in controlling charge transfer kinetics. Of note, easily computed adsorption energies for potential active sites (basal planes, metal-terminated edges, dopant atoms, chalcogen vacancies, etc.) drive the approach of proton reduction energetics to the optimal case of thermoneutrality ($\Delta G_{\text{H}}^* = 0$ eV). While it is well understood that interchanging the M element in MX₂ catalysts will yield predictable electronic structures that vary for basal plane sites versus edge sites in the two-dimensional cases, less effort has been allocated toward understanding the evolution of catalytic reactivity of non-MX₂ chalcogenide active sites.

One example where systematic composition modifications were shown to directly affect catalytic reactivity (Figure 8a,b) is in a recent publication from our group⁷⁸ wherein the chalcogen composition, rather than the M composition, was modulated to engender the binary Chevrel phases (Mo₆X₈, X = S, Se, Te) as more reactive HER catalysts. In this work it was observed that increasing the Lewis basicity of the X₈ chalcogen cage that encapsulates a metallic Mo₆ cluster core (Figure 2) within the structure was effective in reducing overpotentials required to achieve 10 mA/cm² current densities (Figure 8b). It was observed that H* was stabilized at the Mo–X bridging site in all three CPs, with H–X distances being shortest for the sulfide phase, followed by the selenide phase and telluride phase, respectively. Additionally, the sulfide CP in this work was calculated to have H* adsorption closest to thermoneutrality which was found to be in good agreement with our experimental results. Hence, the extension of composition-dependent analyses of non-MX₂ electrocatalysts may be a critical research endeavor for affording insights into the mechanism by which composition modification can improve catalytic reactivity.

4. INTEGRATING INSIGHTS FROM THEORY

The mechanisms by which researchers analyze properties for large composition spaces have dramatically advanced in their sophistication following the advent of computational methods for structure–property prediction. However, this acceleration in materials discovery capability comes at a price. Often, structure–property relationships are developed for multinary systems with a specific functionality in mind (e.g., semi-conductivity, interfacial electrocatalysis, ion transport, etc.) that guides the elucidation of specific descriptors for performance, albeit without considering synthetic feasibility. With few exceptions that include, for example, work by Ceder and Persson et al. in the thiospinel AB₂S₄ (A = Ca; B = Cr, Ti, Mn) family of multivalent cathodes,⁹⁹ chalcogenide material performance tends to be scrutinized without regard for the synthesizability of the materials themselves. The concept of synthesizability is highly complex by nature of its dependence on a multitude of interrelated factors like precursor reactivity, reaction temperature and pressure, and a litany of others. However, we can more easily dissect vast composition spaces by adhering to a working definition of synthesizability as *the tendency of a composition in a specific configuration to exist under a given set of reaction conditions*. For the purposes of practicality, this definition should also specify that said “existence” must be preferential compared to competing reaction products. Nevertheless, synthesizability is, intuitively, a composition-dependent trait that is inextricably linked to the thermodynamic stability of a particular framework. In short, it is often observed that machine learning and DFT-informed approaches efficiently (and often quite accurately) evaluate functionality within complex composition spaces without offering reasonable target compositions for experimental synthesis, or vice versa. While this dichotomy is not in itself an insurmountable barrier for the physical realization of new functional chalcogenide materials, we advocate here for computationally tractable feature regression methods^{100,101} wherein functionality descriptors (e.g., band gaps and positions, electric or thermal conductivities, etc.) can be extracted in conjunction with structure-based descriptors for synthesizability (e.g., formation enthalpies, decomposition enthalpies, and temperature-dependent free energies). Success in this regard will serve to greatly benefit both the experimentally verifiable accuracy of developed computational methodologies as well as the rate at which experimentalists can evaluate computationally identified functionality descriptors for theory-identified target compositions.

4.1. Extraction of Functionality Descriptors. Important considerations when evaluating the performance of any material depend on the desired application, although for the sake of highlighting energy applications for the tunable chalcogenide spaces of interest, here we will consider easily predictable properties related to local coordination and electronic structure.

It is relatively well understood that interfacial catalytic reactivity (i.e., reaction rate and selectivity) depends strongly on local coordination of reaction intermediate adsorbates at active binding sites. In multinary chalcogenides as with any system, these active-site configurations drive reactivity through an “ensemble effect”¹⁰² wherein implantation of unique elements in the proximity of the adsorption site, either via structural incorporation^{79,103,104} or even by electrostatic attraction to a charged species in an electrolyte (in the case

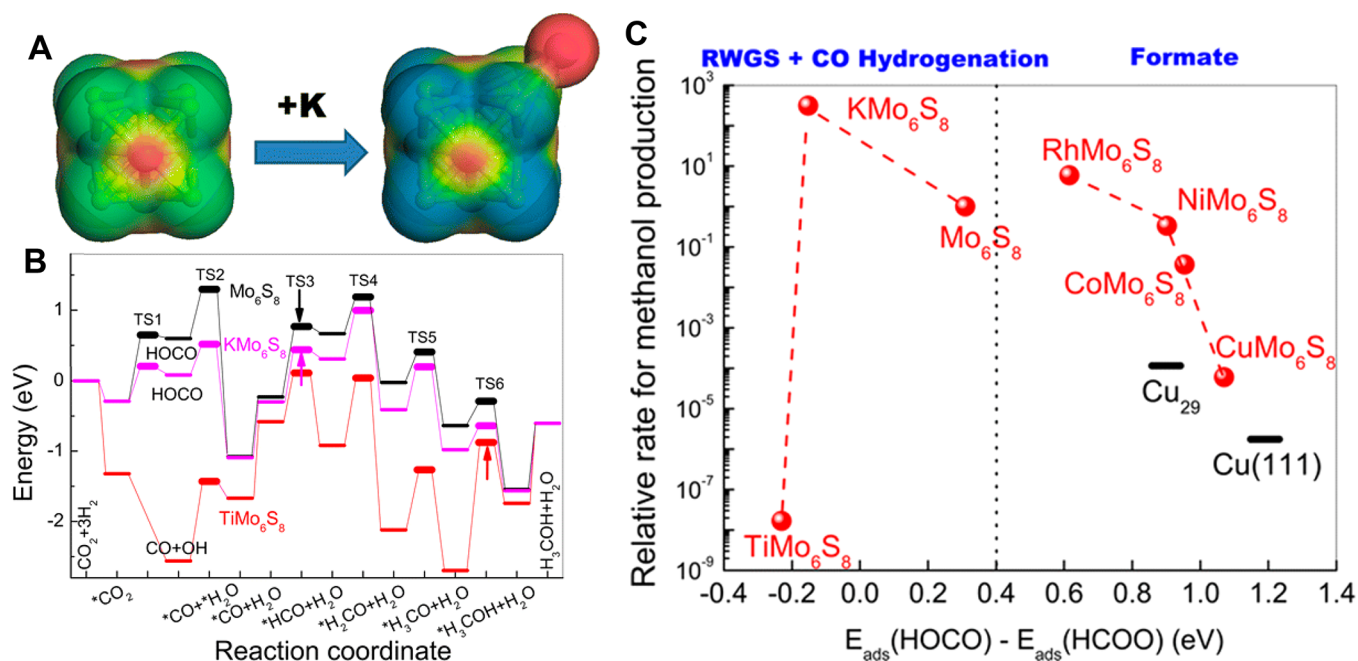


Figure 9. (A) Electron localization in an isolated Mo_6S_8 cluster (left) and a K-promoted Mo_6S_8 cluster (right), highlighting the pronounced electrostatic interaction afforded by inclusion of ternary species into the CP structure. (B) CO_2 reduction reaction coordinate diagram over binary and metal-promoted Mo_6S_8 . (C) Classifications of promoted Chevrel phases according to their preferred CO_2RR pathways. Copyright 2014 American Chemical Society. Figure reproduced with permission.¹⁰⁴

of electrocatalysis).^{105,106} These will both directly affect the local electric field experienced by adsorbates. Moreover, the aforementioned implantation can affect formal coordination to molecular domains of intermediate species, as was previously evaluated by Liu and White et al. over a series of cation-promoted Chevrel phase structures (Figure 9).¹⁰⁴ Intuitively, the evolution of formal bonding between catalysts and reaction intermediates depends on the orbital landscape of the systems involved. This phenomenon has been previously coined as the “ligand effect” to denote electronic contributions from surrounding species to adsorbate binding at the active site (an important consideration in coordination complexes and extended solids alike).^{102,107–109} Hence, we highlight the arguments for and against using the incredibly informative and, historically (for unary metal catalysts), readily computed d-band center model for explaining and predicting reactivity of multinary metal chalcogenide catalysts.^{110,111} The d-band center descriptor is necessarily composition dependent and has proven useful for explaining the reactivity of metallic catalyst systems on the basis of antibonding orbital populations and interactions with adsorbates. However, we must also acknowledge the severe convolution of the frontier orbital landscape of p-block containing systems like chalcogenides. In introducing nonmetal species into multinary chalcogenides, we obviate a potentially straightforward computational mechanism for predicting reactivity. Ostensibly, more complex electronic structure-based metrics for quantifying chalcogenide reactivity must then be addressed, such as the interplay between d-band and p-band positions or, perhaps, the total density of p-states and/or d-states under the Fermi level. These electronic structure descriptors can directly inform new models, for example, of intermediate binding in interfacial catalysis for nonmetal systems where interpretations of the d-band center are less appropriate.

While the challenges in developing “straightforward” descriptors for the reactivity of chalcogenide systems are obvious and will intuitively evolve from one crystal family to the next, the utility in developing system-flexible models where functionality descriptors can be reliably developed will require efficient communication between theory and experiment. Reliable experimental benchmarking of “functional” compositions is key to informing the success of any given computational model with respect to its accuracy in identifying descriptors.

The feedback between experimentalists and theoreticians that we advocate for here will greatly benefit from the additional consideration of synthesizability for computationally identified target compositions, as bench-scale performance testing is often completed at dramatically different time scales than computational predictions. Hence the need for modifications to existing synthetic strategies that tend to depend entirely on the nontrivial thermodynamics and kinetics of the target chalcogenide rather than of the entire multinary system.^{77,112,113}

4.2. Theory Calculations Guiding Stability and Synthesizability. Evaluating the full breadth of multinary chalcogenide composition spaces requires that we understand the limits of synthesizability within any given system. For example, in high-temperature synthetic regimes, we may be unable to access phases that are persistently metastable at milder temperature conditions but that decompose or disproportionate to undesirable mixed phases under more aggressive heating. This is an important consideration owing to the prevalence of high-temperature methodologies in synthesizing many known solid-state chalcogenide materials.

In systems such as the 3-dimensional extended solid $\text{M}_y\text{Mo}_6\text{X}_8$ family, many binary ($\text{X} = \text{Se}, \text{Te}$) and ternary ($\text{M} = \text{Ti}, \text{V}, \text{Cr}, \text{Fe}, \text{Ni}, \text{Cu}, \text{Zn}, \text{Pb}$) compositions are stable and amenable to direct high-temperature (900–1200 °C) synthetic

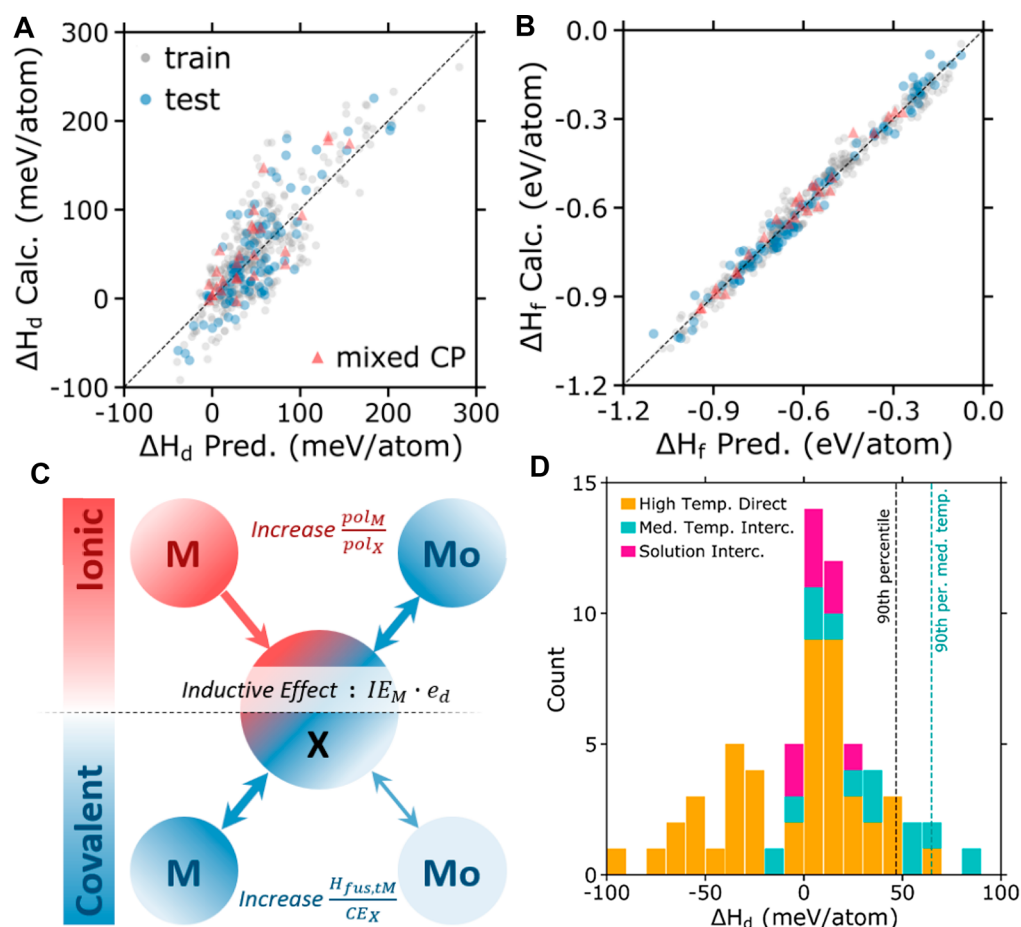


Figure 10. (A) H_δ reproduces CP ΔH_d 's with mean absolute errors (MAEs) of 25 and 26 meV/atom and root-mean-square errors (RMSEs) of 33 and 34 meV/atom for the train (gray) and test (blue) sets, respectively. (B) Predicted ΔH_d 's from H_δ can be converted to CP ΔH_f 's without decreasing accuracy. (C) Multinary CP stability is determined by competing effects of framework ionicity and covalency that are both driven by M–X interactions. (D) Predicted limits for high (>900 °C) and medium (~500 °C) temperature synthesizability based upon calculated decomposition enthalpies derived from H_δ for 67 previously synthesized CP compositions. Copyright 2021 American Chemical Society. Figure reproduced with permission from ref 120.

protocols.^{114,115} However, in the case of some compositions that include the binary Mo_6S_8 structure, persistent room-temperature metastability but high-temperature (>250 °C) instability necessitates indirect synthetic strategies wherein a high-temperature ternary phase (e.g., M = Ni, Cu) is chemically etched at room temperature to yield the metastable binary sulfide phase.¹¹⁶ Additionally, some ternary variations within this system (e.g., M = Bi, Sb¹¹⁷) are neither accessible through etching methods owing to their ternary compositions, nor do they exhibit high-temperature stability. These compositions therefore require moderate-temperature (400–600 °C) solid-state intercalation strategies that implement a prefabricated Mo_6X_8 framework as a synthetic precursor along with a metallic form of the ternary species which is then intercalated during the solid-state reaction.

Such examples of wide-ranging composition-dependent synthesizability are attributable to the complicated nature of bonding landscapes within multinary chalcogenide families. This is largely because competitive electrostatic and covalent interactions determine framework stability in nonobvious ways. We note that this characteristic is also observed for other multinary systems like the ternary metal nitrides wherein component electronegativities have a pronounced effect on the mechanism for stabilizing ternary phases.^{118,119} In these works

by Ceder et al., competing phenomena coined “reductive” and “inductive” effects are described as the propensities for electron redistribution from component elements or component binaries to the bonds of ternary phases having mixed metallic, covalent, and ionic character. The complexity of these bonding interactions, coupled with the expansive nature of multinary composition spaces themselves, motivate our strong emphasis on developing reliable stability models and realistic computational metrics for synthesizability. For example, metrics like decomposition enthalpy should be developed, keeping in mind that, in real systems, competition is between not just elemental species in their standard states but between the entire list of potential binary or ternary side phases that can exist at any given temperature. Hence relying on computationally derived metrics for stability requires that those metrics be borne of appropriate physical models; here, we use the example of formation enthalpy because it is perhaps the most transferrable metric for guiding experimental materials chemists, and it also turns out that favorable formation enthalpies that lie far above the convex hull of a system have the potential to be incredibly misleading, depending on the proposed synthetic route. This is because being thermodynamically stable does not necessarily imply that a composition is the *most* stable in a given chemical system. In other words, high-temperature synthetic routes are

likely to prove unsuccessful if, for example, a ternary material is predicted to be thermodynamically stable but is significantly metastable with respect to its more stable constituent binary phases or even to its competing ternary phases. In such cases, the *more* stable phases under those synthetic conditions will predominate regardless of the apparently thermodynamic stability of the initial target phase.

Stemming from previous work by our group in collaboration with Navrotsky and Musgrave et al.⁷⁷ to explore the driving force for stability in multinary chalcogenide materials that used Chevrel phase sulfides as a case study, we recently incorporated structure-specific insights into a novel feature regression analysis wherein new, stable Chevrel phase compositions were predicted (Figure 10).¹²⁰ In this work the descriptor H_δ for stability was extracted from over 560 000 ML-derived descriptors and was found to accurately predict decomposition enthalpies (Figure 10a) based upon realistic and Chevrel phase-specific properties (Figure 10b) according to the equation:

$$H_\delta = a \cdot IE_M \cdot e_d \cdot \left(\frac{pol_M}{pol_X} - \left(\frac{H_{fus,tM}}{CE_X} \right) \right) + b$$

where IE_M is the average first ionization energy of the cation M in the CP framework, e_d is the number of electrons donated to the Mo_6X_8 cluster by the M species, pol_M and pol_X are the average electric dipole polarizabilities of M and X, respectively, $H_{fus,tM}$ is the total enthalpy of fusion of M, CE_X is the average cohesive energy of X, and a and b are fitted constants. Stability in the case of CP chalcogenides was rationalized in this work by considering H_δ as describing a spectrum of ionic versus covalent M–X bonding. Greater ionicity of the M–X bond (red in Figure 10c) resulted in an increase of Mo–X bond covalency via the inductive effect. The magnitude of this increase was proportional to $IE_M \cdot e_d$ which was found to increase overall CP stability. In this work we also established temperature thresholds at which CP compositions are likely to be synthesizable, which is a critical consideration for experimentalists interested in expanding our understanding of these underexplored materials. Additionally, we highlighted 42 stable yet unexplored compositions which are expected to transition from metallic in nature (<0.01 eV band gap) in certain interstitial configurations of M, to semiconducting (>0.01 eV band gap) in other configurations. Finally, we discovered 83 compositions that should exhibit interstitial M configuration-dependent transitions between nonmagnetic or antiferromagnetic to ferromagnetic behavior. These last two discoveries in particular highlight the potential impact of incorporating thoughtful explorations of potential functionality in tandem with computational stability and synthesizability analyses.

Stability analysis, when viewed simply through the lens of experimental synthesizability, provides an incomplete picture for chalcogenide systems as it does with any material class. Functional chalcogenide compositions can be predicted on the basis of performance descriptors that suggest the composition should have desirable physicochemical properties, and they can be predicted on the basis of their synthesizability. However, very few attempts, if any, have been made to combine models for functionality and stability (particularly operational stability) which, from an engineering and technoeconomic perspective, are both key metrics for any material that tend to dictate long-term operational costs. For this reason, it is especially

important that we understand the interplay between composition and functional stability.

Small-molecule electrocatalysis (e.g., CO_2R , COR, HER, OER, ORR) requires materials that are stable in electrolyte conditions that include specific pH values, electric biases, and ionic compositions—hence, it is critical that the condition-dependent stability of a composition is known. In the case of electrocatalysis, one can point to the Pourbaix stability of a catalytic interface that determines under which conditions a composition can persist.^{121,122} In the example of 2-dimensional chalcogenides, it is known that WX_2 's ($X = S, Se$) exhibit tremendous stability in acidic conditions under applied bias,^{123,124} although other MX_2 's like MoS_2 , which is a preeminent hydrogen evolving catalyst and is even used as protective coating for photoelectrodes owing to its long-term stability in a range of pH conditions, can become unstable with respect to corrosion to form H_2S and HS^- in solution under aggressive applied bias.^{125,126} Examples such as these therefore motivate an exploration of high-throughput methods for determining operational stability of chalcogenides, evidenced by successful work by Gregoire et al.¹²¹ and Liu et al.¹²⁷ in evaluating dynamical changes to chalcogenide materials under electrolysis conditions. Such a high-throughput methodology has already been realized for oxide systems in work by Nørskov et al.,^{128,129} and incorporation of electrochemical stability considerations into computationally derived stability analyses for new electrocatalysts will greatly accelerate the rate at which reliable energy conversion compositions can be developed.

5. CONCLUSIONS

The utility of performing systematic studies that correlate catalytic reactivity to compositional and structural modifications is increasingly apparent for the highly tunable chalcogenide composition spaces discussed herein. Indeed, the modular nature of the composition and dimensionality of multinary chalcogenides like $M_3Mo_6S_6$, $M_3Mo_6X_8$, and MX_2 open many immersive avenues of study wherein foundational chemical insights can inform future iterations of material design. Discussed herein, metal and chalcogen composition-dependent stabilization of surface intermediates is a worthwhile avenue of research, as energy inputs required for achieving industrially relevant current densities in CO_2R , COR, and HER continue to decrease. Structural and morphological effects on the stability and surface reactivity of metal chalcogenides also enable optimization of their energy-conversion performance. Beyond developing “optimally” reactive compositions for energy conversion reactions of interest—an objective that can be achieved expeditiously with iterative communication between theoreticians and experimentalists—researchers are increasing efforts to enable necessary modalities for performance enhancement that leverage the unique properties of chalcogenides specifically. Namely, finite synthetic control over surface structuring, dimensionality, and morphology represents one of the final stages in materials design that precedes deployment of functional energy conversion technologies at the device level. However, much work remains to be done in this composition space in order to unravel a more fundamental understanding of how system-specific properties can affect surface reactivity. Success in this regard will amplify the efficiency with which materials design schemes elucidate novel energy conversion materials.

6. FUTURE OUTLOOKS

Materials researchers are rapidly moving toward the employment of maximally efficient research modalities for extracting new functional compositions. We believe that with an increased emphasis on incorporating metrics for synthesizability into models for predicting new chalcogenide catalysts, closed-loop approaches integrating experimentalists and theoreticians will rapidly illuminate state-of-the-art energy conversion materials. Moreover, real-time analysis of functional energy materials is being facilitated owing to increasing availability and sophistication of correlative operando spectroscopy and microscopy.^{130–132} Consistent growth in this area will serve as a linchpin for experimentally verifying reactivity and functional stability—both of which are properties upon which economic viability depend.

While the development of chalcogenide-based energy materials is a promising route toward transitioning away from fossil fuels to a fully renewable energy infrastructure, many key challenges remain to be addressed. For example, predicting the surface structure and composition changes of multinary catalysts under operating conditions, and subsequently correlating these changes to surface reactivity, is a challenge that may be overcome through the incorporation of computational models that help to interpret and predict the result of operando experimentation.

Lastly, we expect that comprehensively conceptualizing the evolution of physicochemical properties across different chalcogenide structure classes will bolster our understanding of composition–structure–reactivity relationships that are ultimately necessary for guiding synthesis of novel materials.

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Author Contributions

The manuscript was written through contributions of both authors. Both authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

HER, hydrogen evolution reaction; CO₂R, CO₂ reduction; COR, CO reduction; CP, Chevrel phase; PCP, pseudo-Chevrel phase; MX₂, metal dichalcogenide

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