Complexity and Opportunities in Liquid Metal Surface Oxides

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Abstract
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Disciplines
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Complexity and Opportunities in Liquid Metal Surface Oxides

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ABSTRACT: The ability of metal alloys to rapidly oxidize in ambient condition presents both a challenge and an opportunity. Herein, we focus on opportunities buried in the passivating oxide of liquid metal particles. Recently described sub-surface complexity and order present an opportunity to frustrate homogeneous nucleation hence enhanced undercooling. Plasticity of the underlying liquid metal surface offers an autonomously repairing sub-surface hence the lowest E⁰ component dominates the surface unless stoichiometrically limited. This plasticity provides an opportunity to synthesize organometallic polymers that in situ self-assemble to high aspect ratio nanomaterials. An induced surface speciation implies that under the appropriate oxidant tension, the oxide thickness and composition can be tuned, leading to temperature-dependent composition inversion and so-called chameleon metals. The uniqueness of demonstrated capabilities points to the need for more exploration in this small but rather complex part of a metal alloy.

Surfaces and interfaces are ubiquitous across materials. But what is a surface? It depends! For simplicity and brevity, a surface is often defined as the 'exterior', 'outer boundary', or 'termini', hence not part of the material.¹ In this case a surface has no mass and no volume (Gibbs Dividing plane, GDP). In other cases, a surface constitutes a continuum of the bulk only differing by the number density of components (Figure 1a) occupying such a region (Guggenheim Dividing Interface, GDI). Thermodynamically, surfaces are the mass and energy dissipation boundary horizons of any system. Defining a surface solely on mass distribution is, therefore, insufficient. Consider energy distribution, GDP necessitates a duality, in that, transition from one phase to the other will constitute a point in space where two values of energy are feasible, that is an instantaneous jump in energy. This scenario negates any semblance of equilibria hence, is unlikely. The GDI on the other hand, with an increasing concentration gradient (Figure 1b), is challenging to understand for low or high cohesive energy density (vapor pressure) material systems. In crystalline materials, however, one can argue that the lattice planes are clearly defined hence a GDP is an appropriate descriptor. Considering a flat crystalline metallic system at ambient (pressure jump=0, vapor pressure=0), and considering the nature of a metallic bond, then what is on the surface of such a metal? A “sea of electrons” should occupy the surface. Considering quantum mechanics (uncertainty principle), however, defining the loci of surface electrons negates their flux (speed) across the whole material. On the other hand, assuming an energy gradient (GDI) near the surface of an equilibrating mixed material, then autonomous speciation is likely as has been driven by curvature in the Lowengrub-Voigt model² or in thermo-oxidative composition inversion.³⁴ But what governing rules drives the speciation (Figure 1c)? For reacting components, preferential formation of a bond may lead to order and organization over relatively short distances (1-2 nm) as in hydrocarbon self-assembled monolayers (Figure 1d). In more stochastic systems, like formation of passivating oxides on metal alloys (Figure 1a and 1c), redox-driven differentiation occurs over several nanometers.⁵⁶ It therefore follows that, the surface of a material is a very complex part due to its size (nm),⁵⁷ energy profile,⁸ composition, structure, and reactivity.⁹ Focusing on the GDI, we infer that associated surface tension (γ), is a tensor component derived from integration of all local speciation over the whole surface (figure 1e). This equation displays the contribution of the amount of interfacial excess (Γ) for each species (i) and its chemical potential (µi) across the surface distance (x). To understand these ubiquitous parts of metallic materials, we focus on liquid metal systems with an eye on the opportunities this complexity provides.
Liquid Metal Particle: Most metals rapidly oxidize in air to form a thin layer of oxide. What is the surface of a metallic particle (Figure 1a)? One can argue that the thin passivating oxide layer makes up the particle surface, but an oxide is not a metal hence, thermodynamically, it is a different component. So how is this part of the metal, and yet not a component of itself? To define a surface, in this respect, is to look for a set of components that are not part of the object in consideration – and borrowing from set theory, this argument mirrors the Russell’s paradox.\(^8\) It is therefore safe to argue that, though dissimilar, the passivating oxide and the energetically dissimilar interface metal layer constitutes the surface. This definition is analogous to that adopted by others in understanding of interfaces.\(^8,9\)

Is the passivating oxide then similar to self-assembled monolayer (SAM) on coinage metals where the organic and the metal are clearly different entities (Figure 1c)? NO! Unlike the monolayer system that has a definitive linkage point, the Au-S bond for example (Figure 1d), the passivating oxide is a dynamic continuum, emergent from the bulk and a result of an equilibrating system. This relationship would lead to a high-rank tensorial descriptor for surface tension as opposed to the vectorial nature for SAMs (Figure 1c-d). Simplicity in SAMs may, in part, account for why they are widely studied as compared to the surface oxides.\(^14-19\) The governing rules for the establishment of passivating oxide are largely dependent on the environment (temperature, reactive species, pressure, etc), the reactivity of components of the alloy, cohesive energy density (how well the alloy components like each other), diffusivity (hence atomic radius), and thermodynamic state of the bulk. In alloys, how does the passivating oxide emerge and what dictates its composition? Is the passivating oxide layer at equilibrium or, is it metastable like high vapor pressure liquid (e.g. drop of water at ambient)? The low vapor pressure of both the metal and the oxide precludes possibilities for a gradient in concentration which in turn imposes a duality in energy at the metal-oxide interface, suggesting existence of an energy jump across a plane (GDP). What then is the nature of this interface? It follows that there must be some gradient in composition or energy states as we approach the metal-oxide layer from the oxide or the metal side of the interface (Figure 1b). This simple inference poses a challenge in our understanding of these rather small (0.7-5 nm) parts of a material, yet (from an energy point of view) the gradient provides a 'powerhouse' from which the material, as a whole, can be driven to rather unprecedented products or states. The surface, irrespective of the definition adopted, is therefore a metastable region of the material whose energy state(s) can only be averaged from the divergence of the energy states across each point in the surface. At ambient, a diffuse layer of speciated surface material (σ) mirrors an energy gradient between the system (σσ) and its surrounding (ββ), and we infer that this gradient must be dynamic and highly susceptible to small perturbations (Figure 1b). Based on the standard reduction potential of the underlying components, their propensity to flux, and interaction with other alloy component, an equilibrium state is established. Figure 1c illustrates this behavior for BiInSn (Field’s metal). Understanding this surface, therefore, depends on observation length scale, time, and its complexity among other properties. But considering that passivating oxides are larger than most SAMs (e.g. oxide of eutectic gallium indium ≈ 2 nm, while a decanethiol SAM ≈ 1 nm), it is surprising that the literature is scant on their studies. A major hindrance to their exploration is likely the lack of appropriate and affordable tools to capture these subtle differences.\(^8\)

Analogy: SAMs are one peculiar example of thin (nanometer) layer on metal surfaces (e.g. Figure 1d) that significantly alters the properties of the material ranging from work function,\(^19,21\) tribology/wettability,\(^17,22-25\) plasmonic activity\(^15,26-29\) among others.\(^14,16,18,32-34\) This material system has been extensively studied since its first introduction in 1946,\(^35\) whereas the passivating oxide has not garnered similar attention. The SAM can be formed via a thermodynamic driven self-assembly process, resulting in a very ordered structure.\(^36-39\) The deposited thin layer of organic material offers great opportunities in more fundamental areas, most notably structure-property relationship and interfacial phenomena.\(^16,18,23\) As many studies have revealed, the SAM system can be modeled as two interfaces surrounding the bulk (often a hydrocarbon), where each of these three components can be investigated separately by tuning the basic building block, the molecule.\(^40\) The challenge faced by SAM systems, however, is that because of the small size of the molecular component, and effect of...
conformation/molecular orientations, any minor changes in the surface can significantly alter the entire system. Under well-controlled conditions, however, the SAM can be a rather simple system to understand and analyze. Many scholars have, therefore, utilized SAMs to advance technological platforms or reveal unprecedented molecular behavior. The application of SAM can be divided into two types, some applications directly utilize the structure-property relationship of SAM molecule. For example, the monomolecular nature of SAMs lead to their uses in the molecular electronic as well as a candidate in tunable hydrophobic coating. On the other hand, the highly tunable nature of SAMs makes them great candidate platform for building/anchoring other components on metal surfaces.

Whereas SAMs on metals are extensively studied, emerging almost as an independent sub-discipline, metal passivating oxides have not garnered a similar level of interest. Advances in liquid metals coupled with advances in characterization methods has, however, recently highlighted the need to understand, and opportunities in, passivating oxide. By comparing advances in SAMs and how cross cutting their impacts have been, we infer that improved understanding of passivating metal oxides can lead to similar advances in science and impact in functional materials. It is our conviction that the materials community would be equally enriched by a deeper understanding of these nanometer-sized passivating components of metals. Though this is a fledgling field, we illustrate its potential by exploring the limited literature on structure/morphology of the oxides followed by three case studies showcasing their potential uses by limiting our discussion to liquid metals.

![Figure 2. Characteristics of surfaces of liquid metal particles.](image)

(a) SEM image of pristine EGaIn particles synthesized using SLICE method (reprinted with permission from Ref. 3 Cutinho, J., et. al. ACS Nano 2018, 12 (5), 4744-4753. Copyright 2018 American Chemical Society). (b) Depth-dependent distribution of different components across the smooth passivating shell of EGaIn particles determined by XPS (reprinted with permission from Ref. 5 Cademartiri, L., et.al. J. Phys. Chem. C 2012, 116 (20), 10848. Copyright 2012 American Chemical Society). (c) Component distribution map across undercooled Field’s metal particles determine using EDS. (d) HAADF-STEM Contrast inverted image (Sobel filter) to reveal oxide shell thickness. (e) Line intensity profile perpendicular to the line shown in (d).
shows an oxide thickness of ca. 4.6 nm for undercooled Field's metal.

**PREAMBLE: THE SURFACE OXIDE**

Studies of the passivating oxide layer on liquid metal particles have been very limited, in part due to challenges in characterization techniques. This difficulty comes primarily from the compositional complexity within the underlying metal oxide interface over a very small distance. This passivating oxide layer, however, when properly formed and/or engineered provides various advantages to a material. Previous works have empirically shown the complex composition of these interface layer on a liquid binary alloy, eutectic gallium-indium EGaIn (75.5% Ga, 24.5% In), metal particles (Figure 2a-b). On an EGaIn particle, the surface is an ordered layer of adventitious organics, a predominantly Ga$_2$O$_3$ outer surface below which suboxides of both Ga and In are formed (Figure 2b). Presence of a buried InO$_2$ layer captures the stoichiometric qualified statistical mechanics principle of equaling a priori probabilities for both Ga and In to oxidize upon exposure of the bare alloy to an oxidant (Figure 2b).

In non-reacting liquid droplets, curved surfaces of micro- to nano-sized particles bear a sharp energy and compositional gradient(s), that are largely captured through the interfacial excess, $\Gamma$ (Figure 1b) and the Laplace pressure jump condition ($\Delta P = 2y/r$; Where $y$ is the surface tension and $r$ is the radius of the particle). By definition, this sharp gradient serves the critical purpose of establishing both energy and mechanical equilibria between the particle and the surroundings. For metallic droplets, however, exposure to ambient conditions leads to rapid formation of a passivating oxide layer. In metallic alloys, differences in redox potential and diffusivity implies that at time, $t = 0$ of exposure to air, the principle of equal a priori probabilities dictates that all alloy components stochastically oxidize. Immediately after $(t>0)$, a competitive oxidation ensues hence the most abundant, lowest standard reduction potential (E$_0$), and most diffusive component dominates the outer surface of formed oxide. This process, however, implies that a kinetically resolved self-sorting and speciation occurs often resulting in presentation of a unary metal oxide on the surface of metal alloys. This sorting/organization is dominated by, but not limited to E$_0$, stoichiometry, atomic size, cohesive energy density, atomic flux, oxidant diffusivity, temperature and pressure. Upon reaching a certain critical thickness ($d_F$), oxidation becomes infinitely slow and equilibrium is established (approx. 0.7 -5 nm, Figure 2b-e).

Give the principle of equal a priori probabilities, and a thickness-dependent in oxidation mechanism from Cabrera-Mott (<20 nm) to Wagner (> 1 µm), speciation becomes a kinetically driven but thickness-limited process. In EGaIn the surface dominant element is gallium under Cabrera-Mott regime (Figure 2b). Over time, the oxide reaches $d_F$, as flux diminishes, leading to formation of underlying sub-oxides. For a eutectic, selective depletion of some of the alloy components—albeit small, creates an energetically unfavorable hypoeutectic, which induces enrichment of unreacted components at the metal-oxide interface in a manner that counters/mirrors speciation across the oxide shell (Figure 1c, 2b). Sharp compositional gradients, however, presents an interface with a large chemical potential gradient (\$\Delta \mu\$), hence a metastable surface. The $\Delta \mu$ coupled to $\Delta P$, presents a divergence in a stress that inversely scales with the size of the particle. We inferred that such a gradient, affects the properties of the said particle in previously unprecedented way(s) - akin to the SAM, hence can be tuned to bestow new functions to a metal or driven alternate processing pathways. Below, we illustrate the utility of this high concentration of tension via three dissimilar cases.

**CASE 1: METASTABILITY THROUGH SURFACE ASYMMETRY**

Based on our inference on asymmetric energy distribution (high $\Delta \mu$) across the surface oxide, it should be possible to perturb the energy landscape (hence relaxation) in the bulk via the passivating layer. Considering that molten metals have high symmetry (i.e. no order as defined in Landau’s theory), formation of passivating oxides, and the underlying enrichment to maintain bulk equilibrium (e.g. eutectic composition), introduces restrictions on free diffusion as would be expected in a liquid. Seed nucleant (initial) growth must overcome surface tension – this discussion, however, has failed to incorporate any contributions due to a passivating layer. Even after a nucleant seed forms, a competition between growth (reduction of bulk energy) vs shrinkage (increase in surface energy) ensues with the process getting biased to the former with increase in size. Kelton and Greer observed that although role of interfacial energy in inhibiting nucleation is empirically known, its origin remains unknown. Succinctly, they argue that: “The magnitude of the nucleation rate is extremely sensitive to the value of the interfacial energy, variations in $\sigma_0$ (solid-liquid interface free energy) of only a few percentage can alter the predicted rate by several orders of magnitude.” We concurred with this argument, but inferred that a second non-dynamic solid-liquid interface, and associated divergence in free energy, exists underneath the passivating oxide layer. This implies that there are to two solid-liquid interface free energy perturbations that must be overcome for successful nucleant formation—that is, the nucleant interface and the oxide interface. Unlike the dynamic nucleant seed interface where shrinkage is overcome with growth, the structure of the passivating oxide is fixed and cannot be perturbed by the growing nucleant. It follows that, by engineering the surface oxide vis-à-vis miscibility of the bulk (liquid) components, one can significantly influence the growth of a nucleant, especially in a microscale (<10 µm diameter) particle. The passivating oxide, therefore, should lead to significant frustration of liquid-solid phase transformation, hence enhanced undercooling.

Previously, undercooling has been achieved by removing heterogeneous nucleant(s) through, for example, the containerless approach. The containerless approach, however, does not remove homogeneous nucleant(s) – a process that results from structural fluctuations in a liquid, and as such does not exploit the non-
dynamic surface oxide interface tension. It is a perturbation of these liquid-phase fluctuations that we infer can lead to extended arrest of the liquid phase below the melting point.

But it is also well understood that the smaller the particle, the higher the likelihood of undercooling. This size effect is due to the large surface area-to-volume ratio that limits homogeneous nucleation.\textsuperscript{75-78} But what is the role of surface architecture in these size-dependent properties? Considering that Gibbs free energy ($\Delta G$) is expressed as:

\[
\Delta G = \Delta H - T\Delta S + \delta w'
\]

(here $\Delta H$ and $\Delta S$ is the change in enthalpy and entropy respectively, $T$ = temperature and $\delta w'$ = non-PV work), under the right enthalpy-entropy compensation conditions, surface work ($\delta w'$) can dominate $\Delta G$. Whilst the aforementioned methods rely heavily in tipping the bulk enthalpy-entropy balance to manipulate phase transition,\textsuperscript{79-81} $\delta w'$—and in particular surface contributions, is often assumed to be negligible due to entropic limitations. But as inferred above, curved surface are metastable hence a source of significant free energy stress (Figure 1c) that can alter the energy landscape of the bulk (Figure 3a).\textsuperscript{82-86} We infer that, engineering the surface oxide can lead to extension of these size-dependent (surface area-to-volume ratio) properties beyond the nano- into the micro-scale.

The surface work term captures the amount of energy needed to maintain the surface per unit area since $\delta w'$ = $\gamma dA$. Surface tension, by definition is the product of interfacial excess and chemical potential difference, $d\gamma = \sum_{i=1}^{n} \Gamma_i d\mu_i$ (Figure 1e).\textsuperscript{84} The complex composition gradient demonstrated above creates a large curvature-dependent $\mu$ gradient hence, in small particles with large surface areas, the amount of $\delta w'$ can over come the enthalpy-entropy balance and frustrate the liquid-solid phase transition ($\Delta G_{LS} > 0$) even when these perturbations are small, as observed by Kelton and Greer.\textsuperscript{85} But are these perturbations sufficient to overcome thermal fluctuations (thermodynamically, $K_BT$) – hence homogenous nucleant growth, for such processed particles to be of practical use? We infer that the structural complexity of the oxide, when properly tuned, can be sufficient as demonstrated by the long term (years) stability of such prepared particles.\textsuperscript{86} Besides the effect on free energy, formation of a uniformly smooth passivating oxide layer forms a physical barrier to heterogeneous nucleant(s), hence enhances stability of the undercooled state. This understanding enabled synthesis of stable undercooled liquid metal core-shell (ULMCS) particles enabling heat-free solders and a plethora of other ambient or low-temperature metal processing.\textsuperscript{85-88} Since the surface is the main driving force of the metastability, fracture of the oxide shell, whether through mechanical or chemical forces leads to instantaneous flow, coalescence, and solidification (Figure 3b-e). The elimination of heat in the process allows for more versatile approaches in achieving solidification,\textsuperscript{85-86} deposition methods,\textsuperscript{86, 89-90} as well as more choices in substrates for electronic devices. Possible substrates range from flexible substrates like paper or polymers (Figure 3c) to organic, uneven surfaces like roses and other biological surfaces (Figure 3e, h).\textsuperscript{89-90}

This recent development preparation method allowed undercooling of commercially available lead-free solders, SAC 305, achieving liquidous temperature below 100°C as shown via DSC (Figure 3f). This level of undercooling enables low-temperature surface mount and electronic packaging. These low temperature sintering has also enabled biomimetic ‘soft’-lithography on biological surfaces by exploiting self-filtration, capillary densification, and jamming to create solid metal mimics of biological surfaces (Figure 3g). Being soft colloids, whose structures can be arrested via phase change, has enabled understanding of granular matter packing and densification, with new insight expected with continued studies. The soft granular property of these ULMCS coupled with capillary bridge driven sintering (Figure 3d) also enables printing on uneven surfaces, thus achieving a chemical sintered – mechanically reversible printing of surface electrodes. By exploiting particle polydispersity, mechanical bonding (conformal packing and jamming) on biological multi-scale rough surfaces has been achieved (Figure 3h).\textsuperscript{86, 89-90}

CASE 2: CHAMELEON METALS AND AUTONOMOUS COMPOSITION INVERSION

The observed compositional gradient in the distribution of an alloy components across the thin oxide-metal interface implies that under controlled oxidant tension, the structure, morphology, and distribution of surface oxides can be tuned. When the liquid metal particles/droplets are freshly prepared, a thin (0.7 -5 nm) even passivating shell is formed. Heating the particle accelerates diffusion and permeability leading to further oxidation and growth of the oxide layer. A change in oxidation mechanism is expected with thickening of the passivating layer with the initial Cabrera-Mott regime leading to growth of the lowest E° component onto the smooth initial shell (Figure 4a-b). This process is referred to as Expansion-induced Diffusion-limited Oxidation (EDO). Bulk and interface induced thermal stress (pressure), increases as the oxide shell grows with temperature. Stochastic nature of this oxidation combined with volumetric change results in surface texturing upon cooling. At a critical oxide thickness, significant decline in oxide growth is expected unless this oxide shell becomes significantly porous leading to a switch in oxidation mechanism from the Cabrera-Mott to Wagner regime.
controlled oxygen tension, the underlying concentration-differentiated layers effuse through these fractures and oxidize. For brevity, this process is referred to as Thermo-mechanical Fracture leakage and Oxidation (TFO). The leakage of materials, therefore, can be tuned to follow the order of the self-sorted composition of the metal interface below the passivating shell. It therefore follows that the released components will be organized according to their \( E^0 \) value with the lowest component dominating the EDO-regime while the TFO-regime is layered in order of increasing reduction potential (Figure 4a-b). Finally, at much higher temperature, complete oxidation of the particle results in a hollow core.

**Figure 4.** (a) Schematic illustration of TOCI process on liquid Galinstan particles capturing the tunable release of different elements to the outer surface. (b) SEM images validating the mechanism shown in (a). SEM image of (c) pristine binary alloy (EGaIn) particle, (d) EGaIn particle heat treated at 873 K showing only two tiers while, (e) a ternary alloy (Galinstan) shows three tiers corresponding to redox differentiation of the principle component on each tier. Fractal patterns for tier 1 derived from gallium (f), EGaIn (g) and Galinstan (h). All these patterns are \( \text{Ga}_2\text{O}_3 \)-rich but stoichiometry dictates volume and organization. Figures (a,b,e-h) are reprinted with permission from Ref. 4 Martin, A., et. al. *Angew. Chem. Int. Ed.* 2020, 59 (1), 352-357. Copyright 2020 Wiley Publishing. Figures (c-d) are reprinted with permission from Ref. 3 Cutinho, J., et. al. *ACS Nano* 2018, 12 (5), 4744-4753. Copyright 2018 American Chemical Society.

This ansatz has been demonstrated using unary (Ga), binary (eutectic gallium indium, EGaIn), and ternary (Galinstan) systems. Figure 4a schematically illustrates the evolution of the surface components and texture with heating for a ternary eutectic alloy, Galinstan. From the smooth equilibrated shell, we observed effusion of the low \( E^0 \) Ga in fractal like patterns across the surface of the already Ga-rich smooth even surface (Figure 4a-b). For clarity, we false color the two surfaces to highlight the texture. With increased heating, In-rich then Sn-rich features emerge (Figure 4a-b). Similarly, with the binary alloy EGaIn the initially smooth gallium oxide rich shell (Figure 4c-d) is transformed. These particles undergoes EDO and TFO releasing gallium (tier 1) and indium (tier 2) enriched exudates to the surface with concomitant surface texturing (Figure 4d). We refer to this process as Thermo-Oxidative Composition Inversion (TOCI) since the least oxidized element in the oxide shell occupies the highest surface points after TFO. This process continues until majority of the surface is dominated by the tier 2 material (indium). As shown with Galinstan (Figure 4e), increase in number of components in an alloy leads to multiple tiers, from where we infer that this process can potentially continue *ad infinitum*, albeit at different release temperatures, to generate patterned surface oxides (tiers) all dominated by redox-differentiated component of the alloy. This kinetic phenomenon is sensitive to temperature and partial pressure of oxygen, but alloy composition (stoichiometry) dictates proportion of each component. The gradual enrichment and surface patterns derived from TOCI can, therefore, be tuned through alloy design. Figure 4f-h shows changes in surface fractal patterns formed on a unary (Ga), binary (EGaIn, 75% Ga) and ternary (Galinstan, 68.5% Ga) alloy respectively under approximately the same amount of thermal energy. As the number of elements in an alloy increases, smaller and more segregated features, of the same element after EDO, are observed. Pure gallium (Figure 4f) forms the largest, and most dense, oxide island structures likely due to unperturbed uniform oxygen and metal diffusion. As the number of components increase, however, atomic interactions between the elements (cohesive energy density) introduces a barrier to free flow.
metal ions are only partially soluble in the etching medium, atoms from the metal into the surroundings. When the passivating surface oxide generates a controlled flux of concentration. Under controlled etching, therefore, the element should result in regeneration of a similar surface unless under stoichiometric limitations (i.e. too low a concentration). We believe that the plastically deforming metal surface, coupled with high atomic diffusivity in the liquid, allows the establishment of an organized metal underlayer (beneath the oxide), akin to concentration-driven organization on a GDI, allowing the sequential inversion to occur as described above. These observation serves as an indirect evidence that; i) a self-sorting surface oxide is present, and, ii) this surface speciation induces order on the metal layers immediately below the oxide shell hence the proposed underlying $E^0$ driven self-sorting is valid. Relating these observations to case 1 above, one can infer that depending on the thickness of this organized metal underlayer, the structure of the oxide shell will significantly affect the energy landscape of a metal particle especially with decrease in size. The organization inferred here creates a tension (akin to mirror charges) that must be overcome for any Cahn-Hilliard type diffusion to occur – a necessary condition for nucleation and growth. This work on surface oxidation, therefore, further supports the ability to frustrate nucleant growth, hence phase transformation, as discussed above.

CASE 3: NANOBEBN SELF ASSEMBLY

Although the passivating oxides as described above have a rigid order, this is only when viewed at their equilibrium state. Being the bridging layer between, say a liquid metal and air, changes in the surrounding can lead to changes in its state perturbing the established energy gradient. With a liquid core, however, surface plasticity allows the re-establishment of the equilibrium state. This ansatz implies that liquid metal particles, through their oxides, can be a reliable source of specific metal ion(s) even when that component is embedded in an alloy. In a stoichiometric dictated manner, an alloy can also be used to release metal ions in a predetermined manner akin to the TOCI process albeit under an etching (surface subtractive) medium. Since the most reactive components dominates the outer layer of the oxide, it is expected that any process that depletes this element should result in regeneration of a similar surface unless under stoichiometric limitations (i.e. too low a concentration). Under controlled etching, therefore, the passivating surface oxide generates a controlled flux of atoms from the metal into the surroundings. When the metal ions are only partially soluble in the etching medium, a saturated albeit dilute solution is formed (Figure 5b). The steady state, but low, concentration of the metal ions is ideal for autonomous rate/concentration-dependent processes like polymerization, crystallization, and self-assembly. Through felicitous choice of reactants that act as both etchants and ligands (e.g. a conjugate acid-base pair), in situ Heterogeneous Metal/Ligand (HetMet) reaction enables steady state synthesis of organometallic (coordination) polymers (Figure 5a).

When this process is carried out in a solvent in which the chelated metal ion is sparingly soluble, the metal complexes can self-assemble into one-dimensional coordination polymers – that are even less soluble (Figure 5b). Further self-assembly leads to a 3D structure that continues to grow $ad infinitum$ (Figure 5a), leading to high aspect ratio materials (Figure 5d-f). By design, the shape and aspect ratio ($d_1$, $d_2$, $d_3$ in figure 5a) of these materials can be controlled through polymerization ($d_1$) or nature of secondary interactions driving the self-assembly process ($d_2$ and $d_3$). The former is controlled through reaction time while the latter is by engineering the metal coordination sphere—through felicitous choice of metal-ligand pairing. The HetMet derived coordination polymers have dimensions and reaction kinetics that cannot be achieved with traditional batch wise solvothermal methods. The obtained materials assemble into interesting structures, with acetate-base Ga coordination polymers showing ligand interdigitaion upon tight packing. The proximity of the terminal methyl groups is ideal for free radical inter-chain coupling. We inferred that carbonization of the ligands would lead to a carbon coated metal oxide, with the isotropic carbon distribution. The limited number of carbons implied that in absence of sintering, and given proximity of the ligand, that the carbon coating would be graphitic in nature. These self-assembled coordination polymers also, therefore, facile synths and templates for carbon doping on mesoporous oxide through controlled oxidative ligand ablation. Introduction of a conductor (graphene) on the surface of a semiconductor (oxide) leads to gap induced states to balance the large interface dipole (Figure 5d). This leads to bandgap tunability for various semiconducting and opens them up for unprecedented applications such as in catalysis (Figure 5c-d). The ability to perform reactions at ambient conditions permits a larger selection of metal-ligand pairs and thus, greater control over uniformity of the resulting materials (Figure 5e-j). For example, with a slow growth and precipitation, beam like structures can be obtained (Figure 5e-f). We are continuing to explore the dynamics of this process to enable formation of other morphologies such as sheets [thin (Figure 5g) or wide (Figure 5h)], wires (Figure 5i) or tubes (Figure 5j).
As an interface-controlled reaction, HetMet presents additional design handles during synthesis. The stoichiometry of the metal complexes in solution is a function of the oxide composition, solubility, and selectivity of the ligand. Thus, the final composition of the coordination polymers does not necessarily reflect that of the alloy enabling a “trojan-horse” supply of desired metal ions. Inversely, when the etch rate is significantly high, the speciation on the oxide shell dictates the stoichiometry of obtained materials allowing for design of mixed metal coordination polymer precipitates, that can then be turned into mixed oxides. These mixed oxides, like with the carbon doping, enable isotropic doping of semiconductors, leading to unprecedented properties. By understanding the structure of the surface oxide and its evolution with etching, one can therefore envision a programmed multi-metal precipitate(s). Where the coordination ligands bear homologous geometries and are not significantly different in size, co-polymerization can be achieved, otherwise self-sorting occurs leading to multiple products. In conclusion, we infer that HetMet reactions highlights that subtle changes to the structure of the passivating oxide, under the right reaction conditions, can lead to unique materials in terms of their composition, structure and self-assembled morphologies. Post synthesis processing, like selective ligand ablation, leads to unique materials that are realized via an efficient, sustainable, and tunable approach.

Figure 5. In situ heterogeneous metal/ligand (HetMet) reaction for nanobeam synthesis. (a) Schematic illustration of the HetMet process. (b) Concentration profile of metal ion with radial distance from the metal to the precipitate. (c) Schematic illustration of the band structure of β-Ga$_2$O$_3$. (d) Schematic illustration of thermal conversion of assembled Ga-based coordination polymers from (a) into mesoporous graphitic carbon-coated Ga$_2$O$_3$ with corresponding transmission electron microscopy (TEM) images of the respective material. Schematic illustration of changes in the Ga$_2$O$_3$ band structure with creation of induced gap states. (e-f) SEM image of synthesized nanobeams. (g-h) Formation of sheet-like structures. (i) Formation of needle-like nanowires, and (j)
assembly of beams into hollow tubes (gallium oxide). Figures (a-e-f) are reprinted with permission from Ref. 50 Chang, B., et al. Nanoscale 2019, 11 (29), 14060-14069. Copyright 2019 Royal Society of Chemistry (licensed under a Creative Commons Attribution-Non Commercial 3.0 Unported License https://creativecommons.org/licenses/by-nc/3.0/). Portions of the figure were rearranged and letter indication were changed. Figures (b-d) are reprinted with permission from Ref. 93 Chang, B., et al. ACS Mater. Lett. 2020, 2 (9), 1211-1217. Copyright 2020 American Chemical Society.

CONCLUSION/PERSPECTIVE

Passivating oxides, therefore, presents unique capabilities that are otherwise impossible to attain. We highlight only three directions that are made capable by the unique structure of the passivating oxide layer but there is still more to be done. With a better understanding, we anticipate that insights in both fundamental knowhow and new products will be realized. Specific challenges such as the effect of speciation, in the passivating oxide and the metal-oxide interface, on the energy landscape of the bulk are yet to be fully quantified. Similarly, in situ or direct validation of the inferred oxide-induce inverse speciation/organization on the metal layer(s) immediately below the oxide (figure 2b) is desired. Dumeke and co-worker,35 coupled with TOC1-3 and simple charge balance (mirror charge due to surface dipole), imply that this is likely. From a free energy point of view, what are the repercussions of such order and how do we quantify it? There is need to understand, not only the compositional complexity, but also implications to the free energy landscape across materials, especially with respect to particle dimensions. It is therefore important that we understand the nuances of surface layers with their complexities and opportunities, embracing them as pathways to new material products or efficient processing methods. Extension of this type of thinking to other surfaces and interfaces like grain boundaries can lead to validation of new theories, like the landscape inversion phase transformation theory,6,13 or inferences derived from them. Herein, we demonstrate synthesis of heat-free solders, coordination polymers, and chameleon metals via simple approaches – but armed with a deeper knowledge of the passivating oxide surface structure.

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ToC Entry

Due to size and metastable nature, surfaces of materials are often considered an enigma, hence they present technological and scientific challenges in their analysis and/or use. This is more prominent in liquid metals, where complexity in the passivating oxide has largely been ignored. This perspective showcases opportunities emanating from complexity of liquid metal surface oxides as highlighted through a few recent developments.

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