A Perspective on the Catalysis Using the High Entropy Alloys

Nirmal Kumar Katiyar[1], Krishanu Biswas[2]*, Jien-Wei Yeh[3], Sudhanshu Sharma[4]*, and Chandra Sekhar Tiwary[5]*

[1]School of Engineering, London South Bank University, 103 Borough Road, London, SE10 AA, UK

[2]Department of Materials Science and Engineering, Indian Institute of Technology Kanpur, Kanpur, UP, India 208016

[3]High Entropy Materials Center, Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu 30013, Taiwan

[4]Department of Chemistry, Indian Institute of Technology Gandhinagar, Gandhinagar - 382355, INDIA

[5]Metallurgical and Materials Engineering, Indian Institute of Technology Kharagpur, Kharagpur-382355, INDIA

Abstract

The near equimolar and non-equimolar high entropy alloys (HEAs) having five or more major components along with their mingled sites over the surface have made them unique materials for various catalytic reactions involving renewable energies. HEAs provide a platform to tune the surface microstructure and chemistry by selecting and controlling the elements, opening up vistas to design new materials for catalysis. The present perspective aims to provide the correlation between HEAs' structure and catalytic performance in various applications with views on challenges and unique opportunities. The scientific and technological curiosity needs to dig deep into the multicomponent phase space to discover various new materials with unique catalytic properties.

Keywords: HEAs; High Entropy Alloys; Energy materials; Catalytic materials; Multi elements alloy;.

Corresponding Author: Chandra Sekhar Tiwary (chandra.tiwary@metal.iitkgp.ac.in); Sudhanshu Sharma (ssharma@iitgn.ac.in); Krishanu Biswas (kbiswas@iitk.ac.in)

The concept proposed by both Cantor in UK and Yeh in Taiwan, has led to a new class of material, popularly known as "high entropy alloys" and proven to be significantly influential in the design of new materials providing solutions to some of the problems humanity facing today[1, 2]. HEAs' basic advantage over the conventional bi and tri-metallic alloys is the presence of multiple species providing outstanding physiochemical, surface, and electromagnetic properties, including extraordinary catalytic activity with reasonably good stability, which can rather be regulated by tuning the content of each species depending on the need. Initially, HEAs were investigated for the structural materials and inundated with studies to understand the mechanical properties with various alloy compositions[3, 4]. Recent literature shows the potentials of HEAs as a functional material, which could be applied in different areas due to tunable composition as well as emerging new properties. Since, the field is broad and highly unexplored, they will constitute a paradigm shift in catalysis and energy applications by providing a useful handle to discover novel catalysts with improved activity, selectivity, stability *via* intelligent navigation of the vast compositional space and surface microstructure. HEAs are blessed with outstanding properties due to some salient effects associated with multi-principal component nature. Among them, the "cocktail" effect due to the mixing of different atomic species is related to the emergence of unexpected properties due to the cross effect because of the multiplicity of components being present. This can be considered as a warning, saying that we should not expect the properties of HEA as a simple superposition of effect from the individual species. The majority of the HEAs are a combination of transition elements (TM), which are considered prime elements for a variety of catalytic reactions[3, 5], and hence, HEAs are expected to provide improved catalytic activity, which further can be controlled by rational tunning of both composition, geometry, structure and dimensionality. The high value of entropy of mixing due to multiple elements can even decrease the immiscibility gap among alloying elements, making it possible to have

proper control on the concentration of elements in the alloy with the optimization of the catalytic properties. The presence of a large number of elements leads to a humongous number of atomic arrangements or surface microstructure with active catalytic elements, inducing varying modes of adsorption of the reactants and associated intermediates[5, 6]. The presence of elements in atomically mixed form in an alloy can even cause modification of the electronic structure of the individual elements and hence, fine-tuning of the catalytic property. The 'distorted lattice' structure in the HEAs can increase the potential energy of the HEAs, providing a lower potential barrier for adsorption. The catalytic activity and selectivity in HEAs are primarily dictated by the d-band centre model. The electronic structure of HEAs, which can be tuned due by varying composition and strain due to lattice distortion, can be effectively lead to a shift of the d-band in the upward direction, improving bonding between metals and molecules and reducing the adsorption energy for the reactants or intermediates[7, 8]. The huge compositional space allows altering the position of the d-band centres by systematically altering the binding energies of reactants as well as intermediates in a catalytic reaction. Depending on the type of strain field (compressive vs tensile), lattice strain can be tuned by selecting different sized elements to upshift the available d-band center, making it possible for stronger interaction between the metallic components with the adsorbate. In addition, the presence of different metallic elements on the surface (which will depend on surface composition and microstructure) may create a redistribution of surface charges with an alternate arrangement of accumulated and depleted regions. This tunability may allow achieving enhanced selectivity.

Recent investigations on catalytic properties of these multicomponent alloys exhibit a clear indication that notable catalytic activity with excellent selectivity and thermodynamic stability of HEAs, makes them the most desirable material in the near future. Although novel multi-component catalytic materials can be developed by trial-and-error based experimental

approach, it would virtually be impossible to explore the vast compositional space without any screening. Hence, the search for optimum catalysts (chemistry and structure) requires computational techniques, especially 'high throughput' screening *via* machine learning and deep learning. Subsequently, the screened HEAs should be tested to determine whether fine tuning of composition and surface structures is needed. Last but not least, HEAs in the form of nanoparticles or nanosized grains are required for improved activity as the high surface area to the volume provides multiple active sites with efficient material utilization as well as shape effect of the nanosized particles[8, 9]. The reliable synthesis routes for HEAs having five or more elements into nanophases is a daunting task, requiring serious technological development for HEA nanoparticles in years to come. In addition, the effect of shape for various free and integrated HEA NPs warrants research to reap the benefits of stabilization of shapes. Nanostructuring of alloys leads to the surface segregation of some elements, altering the surface chemistry in comparison to the bulk[10], which possesses a caveat for alloy design employing a large number of elements.

At present, precious metals like Au, Ag, Ru, Rh, Pd, Pt, etc. are used as catalytic materials for different reactions to enhance efficiency and yield. However, the noble metals are precious, and their usages are limited with limited tuning capability. In HEAs, varying compositions can modulate the absorption energy of the alloys [11, 12], which presents the innovative solution to reduce the cost of catalytic materials by adding low-cost materials as a diluent. It facilitates the reduction of the activation energy and increases their tuning capability. Recently, the new catalytically active HEAs have emerged using low-cost, highly abundant transition metals elements[13-15], which will be a milestone towards catalytic reactions for renewable energy ($CO_2 \rightarrow$ hydrocarbon fuel). Therefore, the HEAs have full reliance and relevance in catalytic science to prepare a range of catalytic materials for different reactions[11]. In HEAs, designing and tunability can be understood *via* an example such as

the selective reduction of CO_2 into highly reduced hydrocarbons (CH_4, CH_3OH, etc.), requiring a catalyst having a criterion; weak absorption of H and strong absorption CO. Pure Cu follow the same criterion but required high overpotential. In the recipe of high entropy alloy designing, some metals with strong absorption strength of CO and H (Pt, Co, Pd, Ni, etc.); and similarly, some other metals having weak absorption strength of CO and H (Zn, Ag, Ga, Au, etc.) can be selected. Both characteristics need to be incorporated in one single material. Therefore, many combinations by picking elements from both the groups (depicted in **Figure 1 (a)**) can be constituted, which can provide unique bonding sites with optimal absorptions energy to synthesize highly reduced hydrocarbon product as a renewable fuel. Therefore, the cocktail effect (mixing of these metals) might be highly helpful, and there is a vast opportunity to mix different metals and their stoichiometric ratio. Nellaiappan *et al.*[8]have designed a recipe for high entropy alloy material (AgAuCuPdPt), which is highly efficient for CO_2, CO reduction, and hydrocarbon fuel production even at zero potential[7, 16], as shown in **Figure 1**. There are many more compositions with different elements studied the electrochemical catalytic activities such as IrPdPtRhRu[11],CoCuGaNiZn[7], CrMnFeCoNi[17], AlNiCuPtPdAu[18].
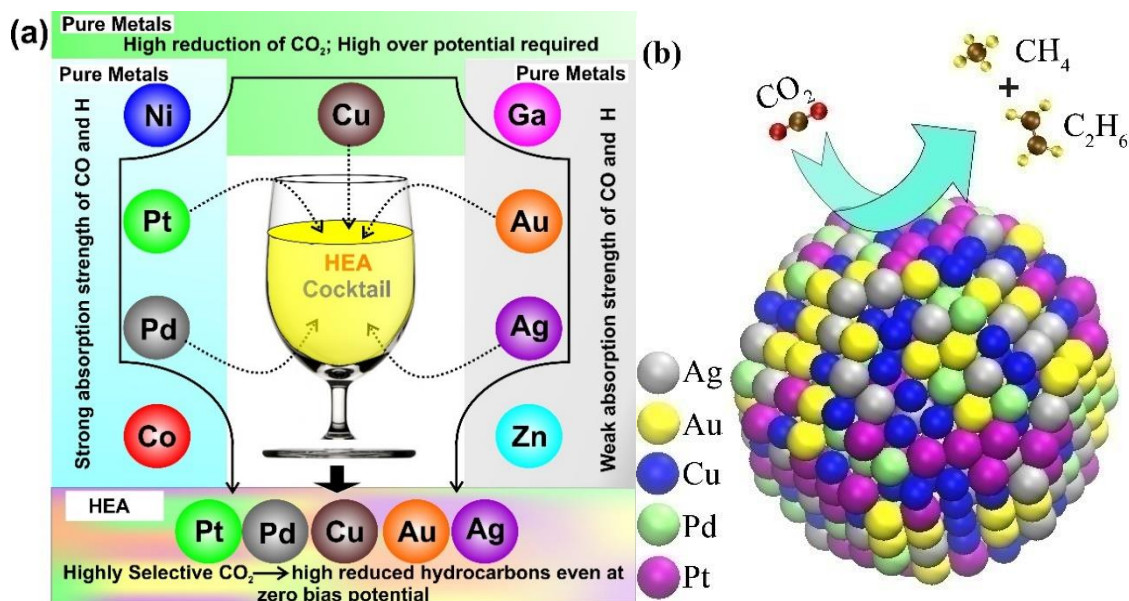
Figure 1: (a) Cocktailing strategies for catalytic material production, (b) schematic of high entropy alloy catalytic nanoparticle.

Hydrogen is considered a greener future fuel, and it has enormous progress in research academia, which could be stored and used for vehicles. In this contestation, HEAs alloys are also being used to study hydrogen storage but with little success. Some compositions were found to store hydrogen 2.5 times higher than its constituents, such as TiVZrNbHf[19], ZrTiVCrFeNi with 1.81 weight percent absorption[20], TiZrNbMoV with 0.59 weight percent absorption[21, 22]. It is to be considered that the higher hydrogen storage in the HEAs is due to its lattice strain, which is imparted by different radii of each metal atom in the HEAs. Most of the conventional materials become highly brittle and may even experience a catastrophic failure upon hydrogen loading. It is due to vacancy stabilization, void coalescence, and localized plasticity. However, this is not with the HEAs; leading to improvement of the ductility and strength[23]; and opening up a new vista for developing strong materials with hydrogen absorption tolerance. Interestingly, the strengthening process is entropy-driven, reducing the stacking fault energy of CoCrFeMnNi (HEAs) on the

absorption of hydrogen. As a result, intense nano-twining on the hydrogen loading increases the strength and ductility or work hardening[23, 24].

The high entropy oxides (HEO) also have been used as electrode materials for reversible energy storage, exhibiting reasonably good storage capacity retention and cyclic stability due to the configurational entropy stabilization effect. The high entropy oxides highly stable in electrochemical response, while medium entropy unstable [Four cations system (medium) configuration entropy (ΔS_{Config}) 1.39R; Five-cations system (high) ΔS_{Config} 1.61R;][25]. In lithiation/delithiation reactions, Li-ions superionic mobility at room temperatures is due to the presence of four-to-five types of cationic atoms randomly occupied, leading to high configurational entropy to stabilize in single-phase rock salt structure at a lower temperature. Therefore, it has a huge scope to adjust the electrochemical behavior by tuning the composition due to multi-cations can be active in the applied potential range. However, the inactive cations in the applied potentials range can retain the rock salt structure or act as matrix. The HEOs are also economical due to low-cost transition metals compared to rare earth metals[26, 27]. Modern electronics gadgets are assumed to be safer with solid electrolytes batteries, but they suffer from low electrical conductivity. Indeed, exploring the possibility with HEO can fulfil the requirement with control of conductivity with higher cyclic stability.

This article intends to describe a future perspective on the role of high entropy materials towards the universality of materials, tunability of materials in the large compositional space, active catalytic sites and impact of machine learning limited to HEA in catalysis.

Summary of the recent reviews

HEAs as catalytic materials is summarized in a few reputed journals (full review, mini-review). Most of the articles have focused on the correlation between functional properties, fabrication and their different applications and future challenges. Tomboc *et al.*[5] have

detailed electrocatalytic behaviour of the high entropy alloys. Authors have stressed the importance of active site determination using advanced experimental techniques; required to establish the relation between electrocatalytic activity and the structure of the HEAs. The computational model needs to understand multicomponent systems' design principle for targeted electrocatalytic reactions[5]. In the same line, Wang *et al*.[28] have pointed out the importance of the high entropy effect (thermodynamics, sluggish diffusion (kinetics), severe lattice distortion (deformation behaviour), synergetic effect) in deciding the activity and selectivity of the HEAs for different catalytic reaction. Amiri *et al*.[29] has presented a recent review focusing on HEAs progress in energy storage and conversion. The excess entropy, electronegativity, valance electron concentration, atomic size, oxidation state are few of the basic factor to be considered for the design of HEAs and high entropy oxides. Xin et al.[30] and Zheng *et al*.[31] describes different kinds of catalytic reactions and preparation techniques and elucidated challenges in the design of high entropy alloys as catalyst materials. Pedersen *et al*.[32] have pointed the importance of the surface chemistry of high entropy materials in relation to catalysis. The determination of surface chemistry by using modern computational tools, including AI (artificial intelligence) will spearhead the discovery of new catalysis. However, such a computation study must be further strengthened with the help of controlled experiments. Moghaddam *et al*.[33] demonstrated a HEAs described the vast compositional space providing us unlimited opportunity to design and developed novel catalyst for specific reactions. Fu *et al*.[34] have laid down some challenges such as atomic disordering in modelling HEAs' surface by DFT and molecular dynamics. The experimental constructing of 3D atomic model of HEAs surfaces will provide an impetus for catalytic research. In summary of all these researches, the development of HEAs materials as functional application and engineering design will grow with time and establish the HEA database as a 'materials genome initiative' to solve many bottlenecks.

Catalysis using high entropy alloys: Dawn of a new class of catalysts

Catalysis research can be revolutionized with the invention of a completely new class of materials. As happened with graphene[35-37], HEAs are one such class of materials that can bring a new revolution in the catalysis research. HEAs are different from the commonly known binary or ternary alloys. In these materials, 5 to 6 metals can be mixed in an appropriate ratio to provide a single phase. Mixing so many entities would increase the lattice distortion in the lattice structure. This happens because all the metallic components have different sizes, chemical bonding and crystal structures. Due to the fact that every lattice point has local distortion, the lattice of HEAs is considered to be severely distorted even local distortion might be small. These intrinsic features of HEAs result in some unique properties such as high mechanical strength, extraordinary fracture toughness, and corrosion resistance[38, 39]. Utilizing these alloys in the catalysis is a relative new area of research. Catalysis is usually governed by high surface area, optimum adsorption energetics, and d-band centre theory. Transition metals have all the correct characteristics making them useful in a variety of catalytic reactions[40, 41]. In principle, if these transition metals are used to prepare HEAs one should harness the various catalytic properties in one material. This concept has a lot of potentials to transform most catalysis research in a completely new way.

Nature of the active sites

There are certain properties in the HEAs, which fundamentally favours the catalytic phenomena. One of them is a unique active site in these alloys. Due to the complexity of mixing so many entities, HEA's surface will be highly heterogeneous. This creates a large number of dissimilar active sites[5, 11, 30]. Such high heterogeneity provides numerous types of sites for a molecule to get adsorbed and react. If the energetics are favourable, HEAs

can show high kinetics compared to singular metals and binary or ternary alloys. For example, Pt alone suffers from the poisoning effect on methanol or formic acid electro-oxidation while its alloy with Ru overcome these difficulties[42-44]. Similarly, Silver binary and ternary alloys have been explored for hydrogen evolution and CO oxidation reaction[45]. Other examples are Rh-Pt bimetallic catalyst [46] and single atom Pt-Cu alloy catalyst[47]. It is also important to note that all the sites present on the surface may or may not participate in the reaction. For example, the nanoparticles of PtPdCuAgAu have been tested for electrochemical reactions, and it has been noticed that Pt dominates in the oxidation reaction and Cu dominates in the reduction reaction [8, 16]. The behavior is quite different from individual Pt and Cu, validating the synergism among the constituting metallic entities. This is quite an interesting phenomenon, and it will be worth to analyse the reason behind such behavior. Although such complex surfaces present an additional difficulty in pinpointing the right kind of active site for a particular reaction, DFT and associated theory calculations can aid in such analysis. The active site performance of PtNiFeCoCu has been determined by calculating the partial density of state (PDOS) using DFT calculation. The Fe-3d, Cu-3d and Co-3d reduce the energy barrier for both oxidation and reduction reaction. However, Ni-3d and Co-3d dominate in the electrocatalytic activity due to PDOS near the Fermi level, while Pt-5d far from Fermi level (E_F) E_V −4.5 eV, serve as the electron reservoir for reduction reaction (HER)[6].

HEAs provides a challenging opportunity to design the material consisting of all kinds of useful active sites. One catalyst will be enough to show a variety of heterogeneous reactions if such materials can be prepared, including liquid-solid, gas-solid, and electrocatalytic reactions. In the single metal case, active sites are limited, giving only a particular type of reaction. Pt for example, is a good catalyst for hydrogen evolution reaction [48] but not so good for oxygen evolution reaction[49]. Ni metal is a good material for oxygen evolution

[50] but a worse catalyst for hydrogen evolution catalyst in comparison to Pt. On the other hand, a recent high entropy alloy composition, PtPdCuAgAu nanoparticles, has shown considerable methanol activity, formic acid electro-oxidation, and CO_2 electro-reduction activity[8, 16, 51]. Thus, this material has excellent oxidation and reduction capability due to its synergetic effect. The universality and synergetics of HEAs as a catalyst have been depicted in **Figure 2(a)**. One can extend its catalytic properties to the liquid phase and gas-phase reactions. If an appropriate catalytic composition is active for all the reactions, the universality of HEAs can be proven. The possibility of such a study needs an interdisciplinary approach with materials scientists, chemists, and chemical engineers working together.
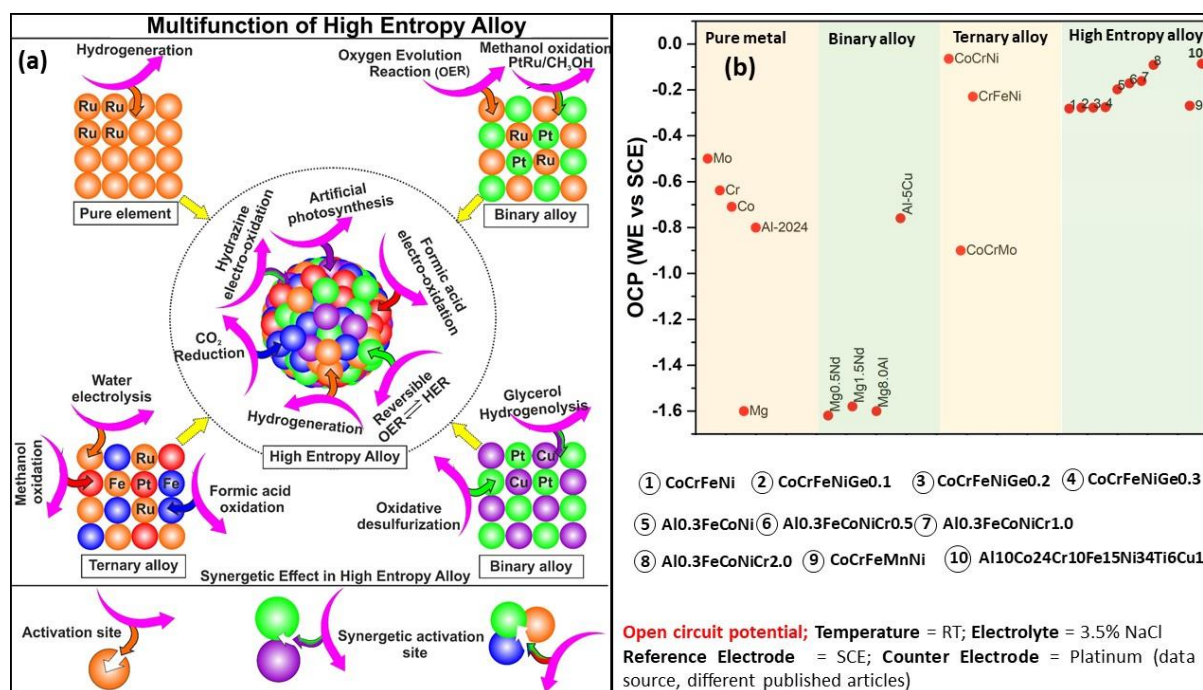

Figure 2: (a) Multifunction of HEAs and their synergetic properties evolution of pure, binary, ternary, and high entropy alloy materials. (b) Open circuit potential of different alloys and high entropy alloys.

A comparative plot of Open circuit potential (OCP) of pure, binary, ternary and high entropy alloys are shown as **Figure 2(b).** We can clearly see the drastic change in the OCP values,

which clearly indicates a change in electron transfer in high entropy alloys compared to pure, binary and ternary alloys. The OCP does not provide an accurate indication as it is dependent on the cell system and conditions. However, the OCP value presented for all materials in similar situations, such as a 3.5% NaCl solution against SCE electrode. These alloy materials are atomically mixed and shifting OCP towards positive as the number of elements increases, indicating the higher stability of the materials and shifting their potential to a more nobler regime or reducing the tendency of catalyst materials rate dissolution. Consequently, the catalyst surface will remain free to accommodates more adsorbates compare to higher dissolution rate materials at particular applied potential. A similar situation occurs with the noble metals (Pt, Au), where they are more resistant to dissolution (oxidation) and accommodate adsorbates over the surface to form the product.

Supported HEAs catalysts

Other big challenge involves the synthesis of HEA nanoparticle supported oxides. HEAs are predominantly prepared by melting-casting or mechanical alloying route, while the oxide supports are prepared by different routes. Thus, it is a challenge to prepare HEAs nanoparticle supported catalysts. Supported catalysts have beneficial economic advantages. The amount of the active metal component used in such catalysts is as low as 0.5 to 1.0 %. This is advantageous as noble metal-based materials can also be used without worrying about cost-effectiveness. While attempts have been made to deposit oxides over synthesized HEAs nanoparticles, these materials are not true supported catalysts as they do not possess the required metal-support interaction. In the absence of this interaction, activity enhancement will be only marginal and not as predicted by Haruta and co-workers[52, 53]. A schematic of the truly supported catalyst has shown in **Figure 3**. This presents an opportunity as well as a challenge to prepare true HEAs nanoparticle-supported oxide catalysts. Extensive research in the preparation methodology should be done; HEAs and oxides are prepared first followed by

the dispersion in a single step combustion or in sol-gel synthesis. However, the stable dispersion of HEA nanoparticles in the precursor solution will be challenging. It is important to assert that in the cases of gas-solid or liquid-solid reactions, catalysis using HEAs will be a technologically viable if and only if they are used in the supported catalyst form. Some of the examples are HEAs supported Al_2O_3, SiO_2, TiO_2, etc. A true supported HEA catalyst will open a paradigm of applications such as, exhaust treatment reactions, methane activation, CO_2 activation, fine chemical synthesis, ammonia synthesis to name a few.

HEO as the catalysts

This is another fascinating area where there is a lots of scope in catalysis [54, 55]. It is known that metal oxides are catalysts for oxidation reaction due to the available lattice oxygen. It will be interesting to see if the similar phenomenon can be invoked and harnessed in HEO. Applications of such HEOs will mostly be in the oxidation processes such as CO oxidation, hydrocarbon oxidation and methane partial oxidation to name a few. In spite if few reports in the literature with name HEO (high entropy oxide) or MEO (multi-element oxide)[56, 57], this area is still in its nascent stage. Synthesis of such materials will be challenging because converting metal to bulk oxides is an energy-intensive process. Pertaining to HEO the Li *et al.*[57] have reported denary MEO nanoparticle preparation (ten metals cations) by Joule heating, using metallic salts; the mechanism of nanoparticles formation combined with temperature-, oxidation- and entropy-driven mechanisms. The heating is fast enough not to allow coarsening of the nanoparticles. Interestingly, the synthesized nanoparticles were obtained single phase and excellent catalytic performance. It is opened large compositional space to designing and tuning catalytic performance with ten metallic cations.

There are two different types of catalyst systems used, such as HEO as a catalyst or catalytic materials (noble metal, transition metal or alloys) supported by HEOs [58], described in a different section.

Metal oxide substituted HEA as the catalysts

Another extremely important class of compounds are substituted metal oxides [59]. In the case of HEAs, one can imagine HEA nanoparticles substituted metal oxide, as a novel composition. Usually, combustion or sol-gel synthesis is utilized for substituted metal oxides. In the case of HEA substituted metal oxide, the HEAs need to be dispersed well in the solvent consisting of nitrate salt of metal oxide followed by gelation or combustion. These materials if prepared will open a completely new dimension in catalysis. These catalysts will have an application similar to supported HEA catalysts.
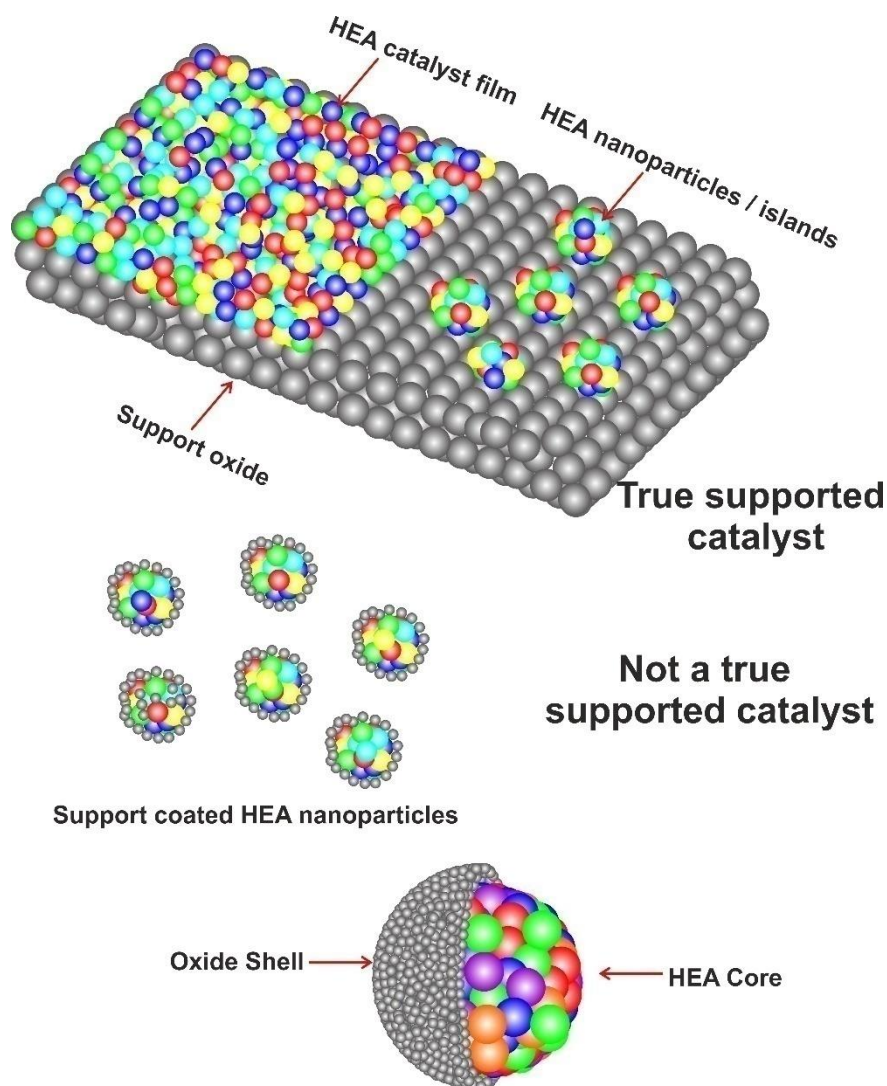
Figure 3: A schematic of distinction in true supported HEA catalyst with not true.

Other than the catalytic supports, semiconducting support such as MoS_2 will also be interesting as these have applications in the sensors [51]. Preparing the graphene supported HEAs is something exciting to investigate. Imagine a single graphene layer on which nanoparticles or HEAs are supported. It is expected that such systems can provide multi-fold enhancement in electrocatalysis. Photoelectrochemistry is another area in which these metallic systems may work; however, the alloy metal particles should exhibit surface plasmon resonance similar to gold, and Ag@Pt (core-shell nanoparticles). It is possible to invent HEA compositions with plasmonic properties for photothermal and photocatalysis[60, 61]. There are some articles that reported HEA NPs SPR resonance in UV range (230 nm –

360 nm)[16, 62] and it is required to shift resonance peak in the visible region to harvest solar energy. This is quite futuristic, but there are chances of success.

HEAs for hydrogen storage is a fascinating area where the phenomenon such as absorption and spillover can be harnessed. The absorption of hydrogen in Pd metal is quite well known which has been utilized for storage as well as purification purpose. Exploring HEA nanoparticles for the same will be an innovative area of research which is still unexplored. For spill over, supported HEA catalysts will be needed and the spill over property can also be explored either for storage or for hydrogen purification.

Computation: Prediction and validation of catalytic compositions and activity

The development of new HEAs necessarily requires "exploring the unexplored vast multi-dimensional compositional space" consisting of elements from the periodic table. The experimental evaluation of millions of alloy candidates is a daunting task, needing the development of an entirely new approach. These possess a problem consisting of rapid screening of an extremely large number of combinations for target properties needed for catalytic applications. This can either be carried by "high throughput experimentation" involving both computational and experimental approaches. However, rapid material development necessitates advanced computation tools, including machine learning (ML) based approaches along with combinatorial methods to create a "materials library" for catalysis, which seem to be appropriate to screen and find the right choice. ML provides new materials compositions designing, solid solution stabilization, and revealing their properties by altering their virtues (shape, size, temperature, pressure, medium, etc). It can also validate the existing composition, phases and their catalytic activity. Combinatorial synthesis involving extremely large number of compositions in one sample with proper compositional gradient for HEAs screened by ML is expected to accelerate the discovery of new catalysts[63]. In the synthesis process, the concept of entropy is a thermodynamics entity, and

their theory is quite established[64]. Therefore, robust software is available to predict the phase, entropy, required temperatures, etc. of multicomponent alloys. It is known as THERMO-CALC having a different version of databases such as TCHEA4, MOBHEA2[65], and continuously getting upgraded. However, its application-based simulation is only in the beginning phase. Ching *et al.*[66] have reported a strong simulated data about the electronic structure and interatomic interaction between all elements in a biocompatible single alloy system. The simulation concept is based on quantum mechanics, total bond order density (TBOD), and partial bond order density (PBOD). It shows the 250 atoms system, charge on each atom, and contribution from each bond interaction in TiNbTaZrMo alloy. It is a breakthrough in high entropy alloy-based simulation for calculating their inner electronic structure and metallic bond interaction in metal's random solid solution. In case of catalytic applications, Pedersen *et al*. [7, 32], and Nellaiappan *et al*.[8] have reported the experimental and theoretical realization of HEAs for their catalytic activity adopting such a route. In the reactions, energy of intermediate and energy of transition state play major role to constitute scaling relation. However, each site can have different metal atoms (hollow sites and top sites). Therefore, energy calculation of sites and their behaviour with the intermediates need to study through computational model as well as in-situ catalysis reaction by liquid cell transmission electron microscopy.

Potential tool to characterize HEA:

The different experimental characterization tools and theoretical simulation become the complementary to decode the complex multielement alloy (HEA). Figure 4 shows different characterization techniques, in which the XRD and EPMA are the bulk materials characterization, while TEM localized area analysis and XPS give surface information of few atomic layers. ICP-MS can be used for trace element or foreign contamination level.
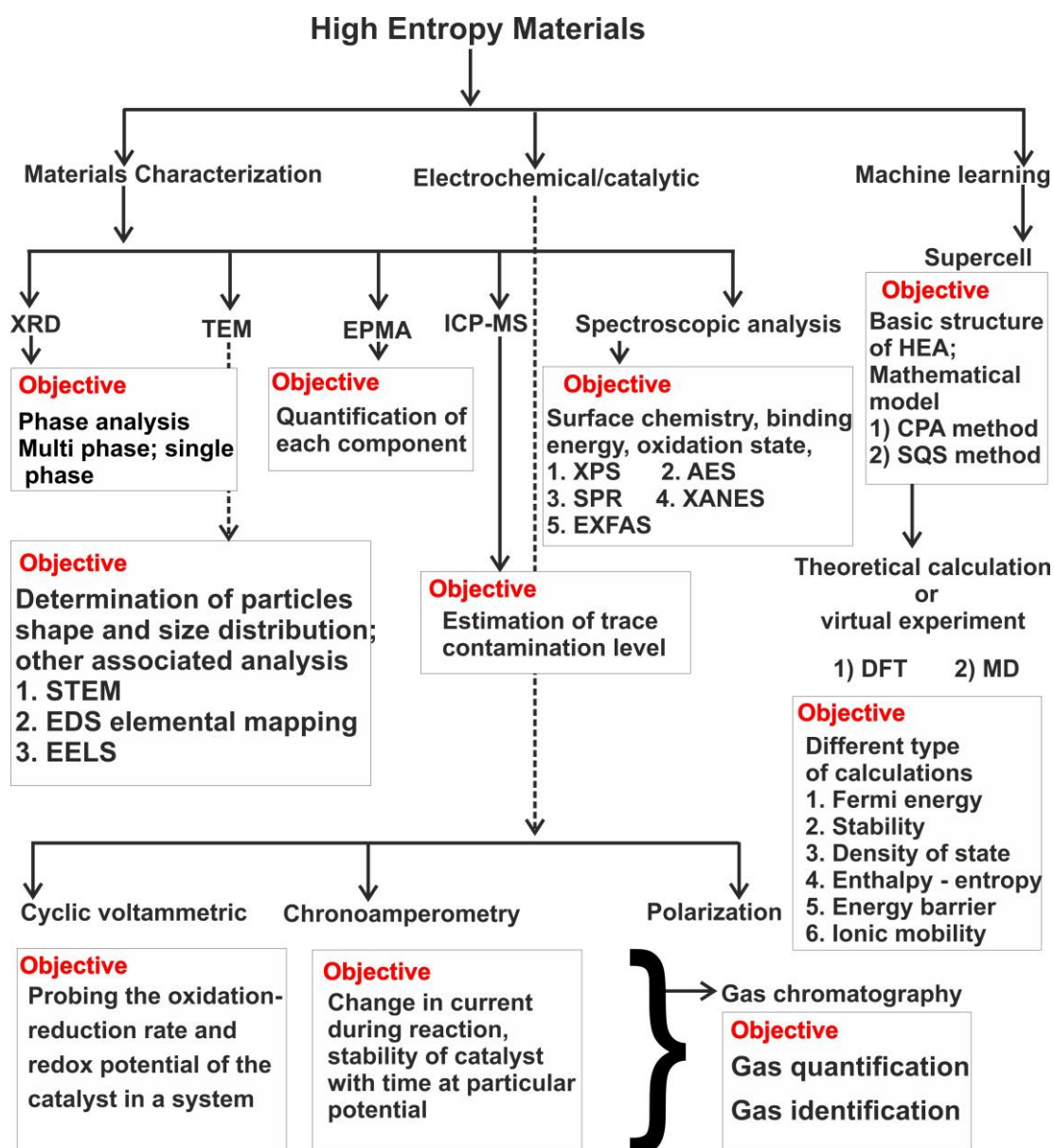
Figure 4: Schematic flow diagram of various characterization tools being used for High entropy alloy (abbreviations: XRD-X-ray diffraction; TEM-Transmission electron microscopy; EPMA-Electron probe micro-analyzer; ICP-MS- Inductively coupled plasma mass spectrometry; XPS- Xray photoelectron microscopy; AES : Auger electron spectroscopy; SPR- Surface plasmon resonance; XANES - X-ray absorption near edge structure; EXFAS-Extended X-ray absorption fine structure; STEM-Scaning transmission electron microscope; EDS- Energy dispersive spectroscopy; EELS- Electron energy loss spectroscopy; CPA -coherent potential approximation; SQS-Special Quasi-random Structures; DFT- Density functional theory; MD- molecular dynamics).

Challenges:

The authors believe that the HEAs have plenty of room for designing new catalyst materials

with low-cost transition materials alternative to precious metals like gold and platinum,

which will surely enhance the efficiency in the coming years. The electrolysis of water using a renewable energy source is one of the best technologies to produce green and sustainable fuel as hydrogen. It becomes possible by enhancement in the understanding of catalytic science. However, there is an absence of a universal catalyst material, which can work for the multi reactions at a time. However, we can approach towards universality using HEA materials as single materials because the catalyst surface has multi-metal atoms persistently warmth-loving dandling over the surface. The d-band theory of prediction catalytic activity and absorption energy of adsorbate must be more robust for HEAs materials, as the HEAs are fundamentally strained lattice and the strained lattice change the degree of d-orbital overlapping, which becomes the cause of shifting d-band centre towards or far from Fermi level. At present, it is a challenge to match the d-band structure theoretically and experimentally due to multielement compared to bi and tri-metallic and required more complex factor to be added for defining and designing the catalytic HEAs for universality.

The nanostructured materials and their shapes play a vital role in the catalytic reactions and their efficiency. However, there are limited methods to prepare HEA NPs in different shapes, demanding new and intelligent processing routes for the synthesis of NPs in large quantities to satisfy the burgeoning need. The wet chemical synthesis of HEAs nanomaterials is difficult due to multi-elemental nature; their salt or precursors have a difference in reaction rate, leading to the formation of intermetallic instead of single-phase alloy formation. Hence, physical routes or a combination of the physical-chemical route may provide the sustainable means for the preparation of HEA NPs. The different shapes like nanoparticles (0D), nanowire (2D), and nanosheets (3D) also have significant advantages in catalytic properties for different kinds of sensor formulation, but at present, it is a challenge to prepare such controlled shapes and required to discover new methodology.

Despite initial surge of design of new multicomponent catalysts, scientific community needs to be ambitious in exploring every breath and depth of higher dimension phase space to discover many new materials by novel design tools. In particular, the surface atoms and their chemical surrounding decide their activity for catalysis. It may be possible to synthesize a single-phase fcc material in which every atomic nearest neighbour is different, leading achieving catalytic potential of all the possible reactions in one material- a dream yet to be achieved.

The Surface plasmon resonance (SPR) is a distinctive property of nanomaterials, which plays a major role in the catalytic reaction specially in photocatalytic reaction. Different elements and their proportion in HEAs can shift their SPR peak in other wavelength regions (UV-Visible). This will be highly beneficial such as like artificial photosynthesis system development. However, yet their not work has been done due to limitation in the preparation of HEAs NPs.

The new generation liquid cell transmission electron microscopy is now a way to explore the nano-chemistry of materials. It can help a deep understanding of HEAs materials as catalyst research. The limitation of free nanoparticle preparation of HEAs is an obstacle in *in-situ* study but *in-situ* electrochemical performance by liquid cell -TEM will open new vistas.

Competing interests:

The authors declare no competing interests.

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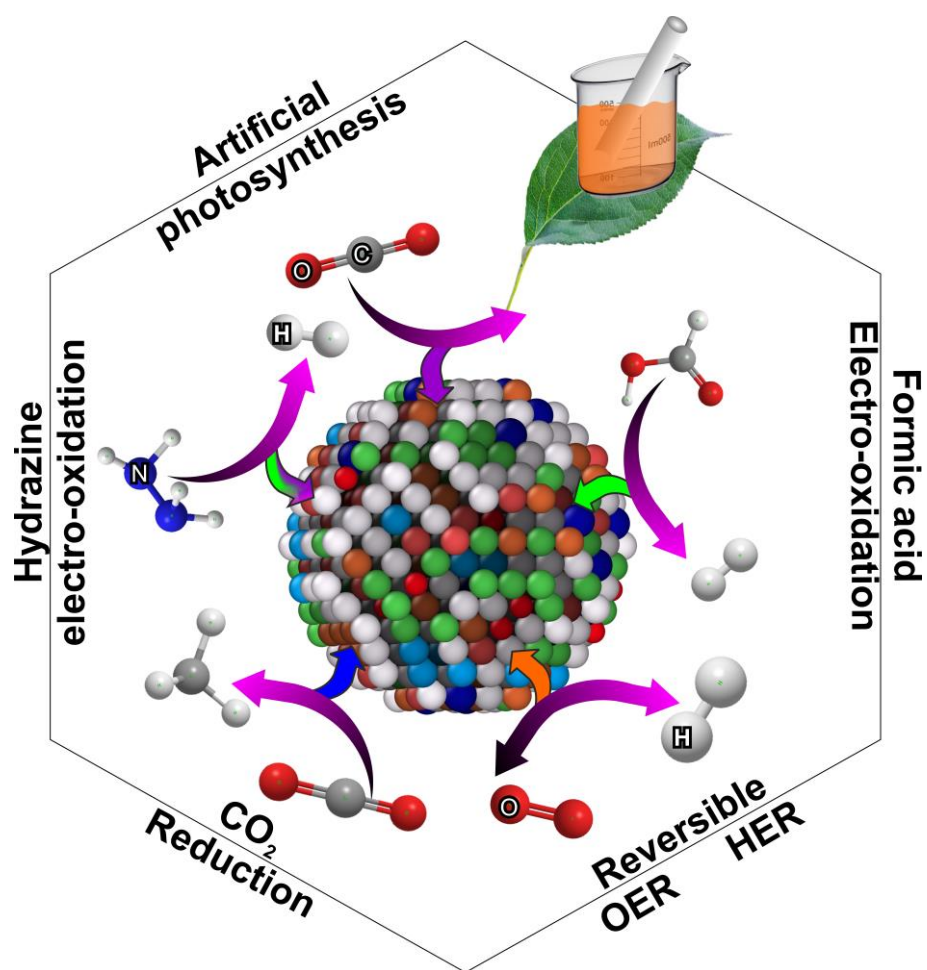from Au@Pt Nanoparticles, Angew. Chem. Int. Ed. 54 (2015) 11462-11466, https://doi.org/10.1002/anie.201505985.

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TOC graphic