Electrosynthesis of high-entropy metallic glass nanoparticles for designer, multi-functional electrocatalysis

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Creative approaches to the design of catalytic nanomaterials are necessary in achieving environmentally sustainable energy sources. Integrating dissimilar metals into a single nanoparticle (NP) offers a unique avenue for customizing catalytic activity and maximizing surface area. Alloys containing five or more equimolar components with a disordered, amorphous microstructure, referred to as High-Entropy Metallic Glasses (HEMGs), provide tunable catalytic performance based on the individual properties of incorporated metals. Here, we present a generalized strategy to electrosynthesize HEMG-NPs with up to eight equimolar components by confining multiple metal salt precursors to water nanodroplets emulsified in dichloroethane. Upon collision with an electrode, alloy NPs are electrodeposited into a disordered microstructure, where dissimilar metal atoms are proximally arranged. We also demonstrate precise control over metal stoichiometry by tuning the concentration of metal salt dissolved in the nanodroplet. The application of HEMG-NPs to energy conversion is highlighted with electrocatalytic water splitting on CoFeLaNiPt HEMG-NPs.
Complex cocktails of dissimilar metals alloyed into a single phase may present advantageous physicochemical properties, such as enhanced tensile strength and increased catalytic activity. Only recently have groups started to alloy five or more elements together into a new class of materials, termed high-entropy-alloys (HEAs). HEAs are generally defined as containing five or more near-equi-molar principle components alloyed into a crystalline solid-solution phase stabilized at an elevated mixing entropy. While the enthalpy of mixing favors phase separation to form intermetallic microstructures, materials with a homogeneous distribution of atoms can be left in a high entropy state under certain experimental conditions. Unique properties arising from the proximal arrangement of dissimilar metal atoms, often referred to in terms of interatomic d-band ligand effects or crystal lattice strain, are of great interest for generating advanced structural and functional materials. While these crystalline materials have been the subject of significant investigation, disordered amorphous materials containing five or more components, termed High-Entropy Metallic Glasses (HEMGs), may also offer access to properties arising from dissimilar metal interactions, though these complex materials remain largely unexplored.

Generally, high-entropy materials are formed by thermal approaches in which compositionally favorable pure metal ingots are liquefied, homogenized, and rapidly cooled to generate the bulk solid material. Translating these planar bulk materials into nanoparticles (NPs) maximizes active surface-area-to-volume-ratio, which directly impacts electrocatalytic efficiency. Though applying high-entropy catalytic nanomaterials to energy-relevant reactions holds great potential, the fabrication of HEA-NPs by a complex thermal-shock method was only recently reported. The application of such high temperatures using these methods necessitates the use of thermally resistant substrates and may incur stoichiometric inconsistencies due to the differences in vapor pressure between molten metals. In contrast to thermal approaches, electrodeposition of metal salt precursors onto a conductive surface constitutes a room-temperature, scalable approach for the formation of amorphous metallic glass films composed of NPs. In addition, the active surface area of electrodeposited NPs may be further enhanced by generating porous or rough particles. For cathodic alloy electrodeposition experiments, variability in NP coverage, size, and stoichiometric composition stems from three main issues: preferential precursor nucleation and growth on energetically favorable sites leading to uneven surface coverage, diffusion layer overlap between neighboring NPs resulting in NP size polydispersity, and variation in precursor electrodeposition potential causing some metals to electrodeposit at higher atomic concentrations.

We recently demonstrated a solution to the issues outlined above by confining metal salt precursors to water nanodroplets suspended in dichloroethane (DCE), allowing for the isolated delivery of a specific number of precursor salt molecules to a localized nucleation and growth domain upon nanodroplet collision with a conductor. In this method, termed nanodroplet-mediated electrodeposition, delivery of the precursor atoms to the substrate results from the formation of a ~10 nm droplet/electrode contact radius upon nanodroplet collision, which we recently explored to observe the nucleation and growth of single Pt NPs in real time on ultramicroelectrodes (UME). In these experiments, we determined that elevated mass transfer (i.e., rapid reduction of chloroplatinate to Pt(0)) within sub-femtoliter (10−15 L) nanodroplets played an integral role in the formation of porous Pt NPs. Interestingly, a 55-ms carbothermal-shock followed by rapid quenching (10⁶ K/s) played an integral role in the first reported fabrication of HEA-NPs by Hu et al. in 2018.

Extending this concept, here we use nanodroplet-mediated electrodeposition to demonstrate that the collision of nano-droplets with a biased electrode represents an electro-shock event on the order of 100 ms, rapidly reducing up to eight confined metal salt precursors into HEMG-NPs with precisely tunable stoichiometric ratios. Furthermore, we use this method to design a CoFeLaNiPt HEMG-NP electrocatalyst for complete water electrolysis to demonstrate the multi-functional potential of this synthetic method.

Results

Electrosynthesis and characterization of HEMG-NPs. Figure 1a shows a representative collision of a single nanodroplet filled with 8 mM CoCl₂, MnCl₂, CrCl₃, NiCl₂, and VCl₃ (40 mM of metal salt in total) onto a carbon fiber UME (rUME = 4 μm). The minimal background current provided by the UME due to its micrometer dimensions facilitates the observation of single nanodroplet collision events. After an initial sharp rise corresponding to the collision of the nanodroplet with the UME, the current decays due to the consumption (electrolysis) of the metal salt initially contained inside the nanodroplet. Importantly, the width of the cathodic peak indicates that electrodeposition is finished within ca. 100 ms, a timescale similar to the one encountered in the carbothermal-shock synthesis (55 ms). The amount of charge transferred during the reduction process, Qred, is obtained by integrating under the blip-type response shown in Fig. 1a. The analysis of multiple independent cathodic peaks leads to an average value of Qred = 3.47 ± 2.68 pC. This amount can be compared to the initial amount of metal precursor contained within a nanodroplet and the corresponding charge, Qini, required to reduce all the precursor ions. According to Faraday’s Law, this charge is given by Eq. 1.

\[
Q_{\text{ini}} = \frac{4}{3} \pi r_{\text{drop}}^3 \sum_{i=1}^{k} n_i C_i
\]

where \( Q_{\text{ini}} \) is Faraday’s constant, \( r_{\text{drop}} \) is the average radius of a nanodroplet, \( n_i \) is the number of electrons involved in electron transfer for the salt \( i \), and \( C_i \) is the concentration of the salt \( i \). Using an average value of \( r_{\text{drop}} = 450 \text{ nm} \), obtained by previous dynamic light scattering and nanoparticle tracking analysis results, we calculated a value of \( Q_{\text{ini}} = 3.53 \text{ pC} \left( Q_{\text{red}}/Q_{\text{ini}} = 98.2\% \right) \). We conclude that all the metal ions initially contained in the nanodroplet are effectively reduced upon collision with an electrode biased at −0.4 V vs. Ag/AgCl (Fig. 1b). For the remainder of this work, we use a higher cathodic potential (−1.5 V vs. Ag/AgCl) to ensure that electrodeposition occurs at or near the mass transfer limit for each depositing species.

Transmission electron microscopy (TEM) was used to investigate the microstructure of binary CoNi NPs electrodeposited at equal stoichiometric ratios (Fig. 1c), giving a selected area electron diffraction (SAED) pattern with diffuse rings characteristic of amorphous material. Probing the atomic distribution within the amorphous microstructure by energy dispersive X-ray spectroscopy (EDX) revealed a disordered cobalt-nickel arrangement. In this work, we demonstrate an important feature of the electro-shock synthesis: precise tuning of NP stoichiometry can be achieved by modulating the ratio of the confined metal salt within water nanodroplets. By adding 20 mM CoCl₂ and 20 mM NiCl₂ to the nanodroplets and analyzing the composition of the resulting NPs electrodeposited onto highly oriented pyrolytic graphite (HOPG) at −1.5 V vs. Ag/AgCl with EDX and inductively coupled plasma mass spectrometry (ICP-MS), we confirmed the stoichiometry of Co₀.₅₆Ni₀.₄₄ was in agreement with the initial stoichiometry of the metal salt dissolved in the nanodroplet. Tuning the proportion of CoCl₂ and NiCl₂ facilitated the generation of Co₀.₃₅Ni₀.₇₅ and Co₀.₇₅Ni₀.₂₅.
MG-NPs with high precision, which were also verified by ICP-MS (Fig. 1d, Supplementary Table 1). Importantly, ICP-MS data were perfectly aligned with EDX quantification despite the greater uncertainty in EDX measurements, as indicated in Fig. 1d. These results stand in stark contrast to the stoichiometric variation within a CoCrMnNiV film electrodeposited from an aqueous solution containing 20 mM aliquots of each precursor metal salt onto a glassy carbon electrode biased at −1.5 V vs. Ag/AgCl. The resulting EDX maps reveal a preferential co-deposition of a CoNi-rich phase and separate CrMnV phases (Fig. 1e). Using nanodroplet-mediated electrodeposition, the stoichiometry of the CoCrMnNiV NPs can be controlled to near-equimolar ratios, as shown by EDX and validated by ICP-MS, maximizing the mixing entropy (Supplementary Fig. 1). Typical electrodeposition and electroplating methods employ chemical additives, such as polyethylene glycol or hydrochloric acid, to obtain a desirable microstructure, which must be optimized based on the metal salt composition. In this generalized method, confining metal salts to water nanodroplets appears to mitigate the phase-separation effects, as NPs formed by electro-shock reduction maintain the disordered structure and intended stoichiometry shown by EDX and ICP-MS over a wide variety of metal compositions (vide infra). It is worth noting that typical lithographic methods used to generate complex alloy nanomaterials incur up to 50% variability in stoichiometric control. Furthermore, this method allows precise stochiometric control within 2–5%. ICP-MS results confirm the presence of TBA+ across the oil/water interface. An amorphous microstructure is confirmed by a lack of crystallinity at high resolution and the presence of diffuse rings on the SAED pattern. Correlated ICP-MS and EDX results on Co0.5Ni0.5, Co0.25Ni0.75, and Co0.75Ni0.25 MG-NPs confirming precise control over NP stoichiometry. Alloy film electrodeposited from an aqueous solution of equimolar metal salt precursors demonstrating phase and stoichiometric heterogeneity. Source data for panels a and d are provided in the Source Data file.
Design and application of a multifunctional HEMG-NP electrocatalyst. We demonstrate the versatility of the electro-shock method and its application to designer, multifunctional electrocatalysts by synthesizing a novel CoFeLaNiPt HEMG-NP electrocatalyst for cathodic and anodic water splitting. Generally, electrocatalysts are synthesized and optimized for a particular electrocatalytic reaction. However, it may be economically beneficial to design nanomaterial electrocatalysts amenable to multiple electrocatalytic reactions, a task which is streamlined by the synthetic method presented in this work. For instance, two important reactions for the production of fuel cell reactants are the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER). Although Pt offers facile kinetics for the HER, it displays rather poor performance for the OER. Furthermore, metal oxides (MOx) and oxyhydroxides, such as CoOx, FeOx, NiOx, and mixed MOx, such as NiFeOx, have been shown to be kinetically favorable toward the OER; however, each of these MOx compounds have poor activity toward the HER. Rare-earth oxides, such as La2O3, have been used to confer stability to materials exposed to alkaline conditions. The literature precedent surrounding these materials inspired us to design a CoFeLaNiPt HEMG-NP electrocatalyst amenable to the OER and the HER at a single nanomaterial. It is important to note that the calculated entropic contribution to the total Gibbs’ free energy of the NP arises from near-equimolar elemental concentrations, whereas colloidal alloy systems generally contain a single principle element doped with other metals in low concentration. Electrocatalytic activity may be greatly amplified by tuning the stoichiometric ratios, as was reported for the record oxygen evolution activity of Fe0.23Ni0.75 oxyhydroxide materials. Because the high-entropy classification is predicated on the equimolar ratio of the elemental constituents, it may be necessary to tune metal ratios away from the high-entropy state to optimize electrocatalysis. In this work, it is our goal to explore the near-equimolar synthesis of HEMG-NPs using nanodroplet-mediated electrodeposition and demonstrate the precise tuning of metals rather than to search for an optimal stoichiometric ratio for electrocatalytic water splitting.
Accurate determination of the electrochemically active surface area (ECSA) for a given material is extremely important to quantify and compare electrocatalytic activity. Commonly, the double layer capacitance of the catalyst is determined by CV in a non-faradaic region or by electrochemical impedance spectroscopy (EIS)\(^4\). After electrodeposition of CoFeLaNiPt HEMG-NPs onto the HOPG substrate at −1.5 V vs. Ag/AgCl, CV at seven scan rates was conducted (Fig. 3a). Plotting the cathodic and anodic current as a function of the scan rate revealed a linear function, where the slope indicated the double layer capacitance (CDL). EIS can also be used to obtain the double layer capacitance by fitting the impedance response of the system at different frequencies to the Randles circuit (Fig. 3b). The double layer capacitance can be correlated to the ECSA using the specific capacitance of the material, and further details of this analysis can be found in the Materials and Methods. Using CV and EIS, we determined the ECSA of the CoFeLaNiPt HEMG-NPs to be 0.0013 and 0.0041 cm\(^2\), respectively. Nanodroplet-mediated electrodeposition offers an additional metric for approximating the ECSA through an integrated form of the Cottrell equation to determine the total number of NPs incident on the electrode surface over a certain deposition time (t), given by:

\[
\text{Coverage (NP/cm}\^2) = \frac{2C^*Dn^{-1}t^{-\frac{1}{2}}N_A}{m^2}
\]  

where \(C^*\) is the concentration of nanodroplets suspended in DCE, \(D\) is the nanodroplet diffusion coefficient as determined by the Stokes-Einstein relationship, and \(N_A\) is Avogadro’s number. This analysis approximates NP coverage based on diffusional mass transfer of nanodroplets to the electrode surface with subsequent electrodeposition to form a single NP, which was previously validated for Pt NPs electrodeposited from water nanodroplets\(^2\). By assuming a hemispherical geometry and using the average NP radius of 320 nm determined by SEM, an approximate ECSA was calculated as 0.012 cm\(^2\), as shown in Fig. 3c. For the analysis of our electrocatalytic materials, we used the average of the ECSA values determined by these three methods (Supplementary Figs. 6–17).

We chose to evaluate these electrocatalysts in 0.1 M KOH due to increased metal oxide stability\(^5\), reduced cationic interaction\(^6\), and practicality for real-world water electrolysis applications\(^7\). Resulting \(iR\)-corrected linear sweep voltammograms at 10 mV/s given in Fig. 4 highlight HEMG-NP functionality for both the HER and the OER. Electro catalyst overpotential (\(\eta\)) is most often reported as the difference between the applied potential (\(E\)) and the equilibrium potential (\(E_{eq}\)), which is 1.23 V vs. RHE for the OER and 0 V vs. RHE for the HER\(^8\). Using this metric at a current density of 10 mA cm\(^-2\), we obtained an OER overpotential of 377 ± 4 mV for the HEMG-NPs. Significantly, this finding represents a 139 and 36 mV improvement over unary Fe and Ni, respectively, demonstrating synergistic transition metal oxide interactions\(^9\). The HEMG-NP overpotential also corresponds to typically reported values for IrO\(_x\), a benchmark OER electrocatalyst\(^10\). For the HER, the HEMG-NPs significantly outperformed the individual components with an overpotential of 555 ± 2 mV, representing an improvement of 132, 176, and 183 mV over Fe, Pt, and Co NPs, respectively. Though these HER overpotentials are slightly elevated compared to a benchmark OER electrocatalyst\(^15\). For the HER, the HEMG-NPs significantly outperformed the individual components with an overpotential of 555 ± 2 mV, representing an improvement of 132, 176, and 183 mV over Fe, Pt, and Co NPs, respectively.
for the electro-shock method to generate novel electrocatalysts, increasing the overall electrocatalytic efficiency of these materials requires optimization. The HEMG-NP electrocatalyst was found to be stable for at least 1 h at an overpotential necessary to produce 10 mA cm\(^{-2}\) for both the OER and the HER (Supplementary Fig. 19). Furthermore, metal loading on the substrate as a result of the nanodroplet-mediated electrodeposition method was on the order of 10 ng cm\(^{-2}\) for each material, constituting a significant reduction in mass compared to typically employed water splitting electrocatalysts. Other electrocatalytic parameters derived from this analysis, such as mass activity and Tafel slope, can be found in Supplementary Table 3. In this work, it is our intent to showcase a generalized platform for the design and synthesis of novel catalytic multi-component materials. To this end, we present the CoFeLaNiPt material as a successful example of an electrocatalyst specifically designed for both the HER at Pt active sites and the OER at transition metal active sites, which happens to show interesting synergistic activity above that of its individual components. In principle, the ability to functionally and stoichiometrically tune activity by varying metal salt species and ratios within water nanodroplets offers exciting opportunities for many electrocatalytic systems.

**Methods**

**Reagents and materials.** All chemicals were of analytical grade unless noted otherwise and used as received. Dichloroethane (DCE, 99.8%), tetrabutylammonium perchlorate (TBAP, 99%), sodium dodecyl sulfate (SDS, 99%), hexachloroplatinic acid, and iron (III) chloride were obtained from Sigma-Aldrich and used without further purification. Chromium (III) chloride, cobalt (II) chloride, manganese (II) chloride, vanadium (III) chloride, nickel (II) chloride, indium (III) chloride, cobalt (II) nitrate, nickel (II) nitrate, lanthanum (III) nitrate, iron (II) nitrate, platinum (IV) nitrate, and gadolinium (III) chloride were obtained from Fisher Scientific and used without further purification. Stock solutions (100–300 mM) of each metal were prepared in MilliQ water (>18 M\(\text{cm}\)) and diluted as necessary to be used in the emulsion preparation. Metal salt solutions were stored in a dark refrigerator (4°C) to avoid photodecomposition. Metal salt compatibility was investigated to prevent competing reactions (Supplementary Table 4). Metal salts were analyzed by UV-vis spectroscopy to ensure no leakage into the DCE phase following sonication (Supplementary Fig. 20).

**Instrumentation.** The electrodeposition experiments were performed using a CHI model 601E potentiostat (CH Instruments, Austin, TX) using the Amperometric i-t Curve technique. Rotating disk electrolysis and electrocatalytic analysis were performed with a WaveDriver 200 and WaveVortex (Pine Instruments, Durham, NC). A 3-mm radius glassy carbon rod was used as the counter electrode. To decrease the risk of silver leakage from the reference electrode, we employed a double-junction Ag/AgCl electrode modified with a home-built 3.5 M KCl, 3% w/w agarose salt bridge. No obvious junction potential or other deleterious effects could be observed in the cyclic voltammogram of 1 mM ferrocene methanol in a 0.1-M KCl aqueous solution as a result of the double-junction reference. In addition, we have found this material to be stable in DCE for over two months. The emulsion was prepared using a Q500 ultrasonic processor (Qsonica, Newtown, CT) with a \(\frac{1}{4}\)" microtip probe. A V-650 UV-vis Spectrometer (Jasco, Oklahoma City, OK) was used to quantify metal salt leakage from the aqueous emulsion phase to the continuous DCE phase. SEM images and EDX spectra were acquired using a Helios 660 Nanolab Dual Beam System (FEI, Hillsboro, OR) and INCA PentaFET -x3 (Oxford, Abingdon, United Kingdom), respectively, at 30 keV and 0.69 nA. TEM images and diffraction patterns were collected using a 2010F-FastTEM (JEOL, Peabody, MA) with a zirconated tungsten thermal field emission tip at 200 keV. X-ray diffraction (XRD) spectra were collected using a Rigaku SmartLab X-ray diffractometer (Rigaku, Tokyo, Japan) in a 2θ grazing angle configuration. Inductively coupled plasma mass spectrometry (ICP-MS) data were collected using a Nexiso 300-D ICP-MS (Perkin Elmer, Waltham, MA). HAADF-STEM and diffraction images were collected with a Talos F200X G2 (FEI, Hillsboro, OR) at 200 keV using a single-tilt holder.

**Nanodroplet-mediated electrodeposition procedure.** HEMG-NPs were electrodeposited on HOPG or glassy carbon substrate electrodes from a water-in-oil emulsion system, as previously described\(^5\). In brief, a 30-μL aqueous phase containing a total of 40 mM metal salt precursor ions was suspended in a 5-mL DCE continuous phase. The application of a chloroform or ionic liquid continuous phase has also been explored\(^5\). TRAP (0.1 M) was added to the DCE phase as a non-aqueous supporting electrolyte and charge balance mediator. The resultant two-phase solution was subsequently ultrasonicated (500 W, amplitude 40%) using a pulse mode method (3 s on, 5 s off, 6 total cycles) for emulsion formation. Following sonication, a three electrode electrochemical cell was inserted into the emulsion and biased at a potential sufficient to reduce metal salt precursors at the
recorded following diffusion and subsequent reduction at a carbon electrode). Individual current transients for attoliter nanodroplet collisions were recorded following diffusion and subsequent reduction at a carbon fiber UME. For NP morphology and elemental composition characterization experiments, the electrodeposition was carried out on a 3-mm HOPG disc electrode secured in a Teflon cell with a Viton O-ring. The substrate was exfoliated and rinsed with ethanol prior to emulsion loading, and the post-deposition substrate was rinsed with ethanol and water prior to characterization.

**Electron microscopy and energy dispersive spectroscopy analysis.** Single HEMG-NP images and energy dispersive spectroscopy (EDX) spectra were acquired using a Helios 600 Nanolab Dual Beam System (FEI, Hillsboro, OR) and INCA PentaFET-x3 (Oxford, Abingdon, United Kingdom), respectively, at 30 keV and 0.69 nA. High resolution elemental mapping for semi-quantitative metric analysis of individual HEMG-NPs was collected at 30 keV and 11 nA for up to 10 min of continuous EDX scanning to enhance signal-to-noise ratio while minimizing drift in the SEM. EDX maps were brightness and contrast adjusted and false-colored to demonstrate homogeneous elemental distribution within single HEMG-NPs. Atomic resolution HAADF-STEM/EDX maps were generated using a SuperX Energy Dispersive Spectrometry system (SuperX EDX) with four Silicon Drift Detectors (SDD). Molybdenum grids coated with amorphous carbon (Ted Pella, Redding, CA) were used to support HEMG-NPs for TEM analysis to avoid competing Cu signal during EDX analysis.

**X-ray photoelectron spectroscopy and X-ray diffraction analysis.** XPS spectra were obtained under UHV with a base pressure of 5 × 10⁻⁹ torr on an Axis Ultra DLD with a monochromatic Al Ka source coupled with a hemispherical analyzer. High resolution XPS spectra were baseline subtracted with a Shirley background correction method for subsequent individual peak fitting and peak identification. High coverage HEMG-NP samples were electrodeposited on a glassy carbon rotating disk electrode (r = 2.5 mm) at 1000 rpm and −1.5 V vs. Ag/AgCl and subsequently rinsed with ethanol and water prior to analysis. High substrate coverage was confirmed via SEM prior to surface characterization by XPS. XPS survey scans indicated the presence of characteristic carbon and oxygen peaks consistent with the underlying glassy carbon substrate electrode. XPS survey scans and high-resolution element scans are presented in the supplementary information for two representative quinary HEMG-NP systems indicating the presence of metal oxide species. XPS peak identification of high resolution regions was achieved by comparing binding energy and peak splitting values with standard literature values. These high coverage samples were subsequently analyzed with a Rigaku Smartlab XRD in a 20 grazing angle orientation to confirm the amorphous microstructure.

**Inductively coupled plasma mass spectrometry analysis.** Stoichiometric analyses for high coverage HEMG-NP samples were obtained using a Nexodia 300-D ICP-MS to supplement EDX analysis for single NPs. High coverage CoNi HEMG-NP samples were prepared by electrodeposition on a glassy carbon rotating disk electrode (d = 5 mm) at 1000 rpm and −1.5 V vs. Ag/AgCl. NPs were extracted with concentrated nitric acid and diluted to 5% v/v acid solution in water prior to ICP-MS analysis.

**Electrocatalytic analysis.** Electrocatalytic analysis was carried out using a Pine WaveDriver 200 and AfterMath software in a temperature-controlled (25 °C) Pt-mimetic surface. For electrocatalysis on extended and nanoscale Pt-mimetic alloy surfaces. Nat. Mater. 6, 241 (2007).

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