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# Title: Flame synthesis achieves compositionally tailorable high-entropy metal-containing nanomaterials

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**Abstract:** High-entropy metal-containing nanomaterials have garnered interest in diverse fields such as electrocatalysis and energy conversion. Their synthesis typically requires high temperatures (e.g., >1000 K) to facilitate homogeneous mixing and rapid transformation of metal precursors. However, current state-of-the-art approaches typically involve complex reaction environments and require specialized equipment/operations. Herein, we demonstrate a versatile flame synthesis process to fabricate high-entropy metallic single atoms and/or nanoparticles supported on soot-like carbon via blending organometallic precursors into fuel (namely, paraffin wax) and subsequent burning. The high flame temperature (~1800 K) enables strong metal–carbon association with tailorable chemistry and homogeneous bonding between dissimilar metallic elements (up to 25 metals studied), regardless of their thermodynamic compatibility. Additionally, we show high-performance electrosynthesis of hydrogen peroxide to highlight this approach as a promising method for electrocatalyst development.

## Main Text:

## Introduction

Integrating different elements into a single particle can unlock potential for advanced materials in the fields of catalysis, bio–nano engineering, and energy conversion and usage (*1-3*). For example, it has been reported that high-entropy metal-containing nanomaterials (HMNs) (*4-7*) with at least five metal species in a single nanoscale material (*8-10*) display synergistic and cooperative properties that are superior to those displayed by single-metal systems in many catalytic processes (*11-14*). Although homogeneous mixing and alloying are essential for the synthesis of HMNs, these are difficult to realize because new equilibrium high-entropy states need to be achieved and maintained when alloying elements with different atomic, electronic, or physiochemical properties (Supplementary Tables 1 and 2 and Supplementary Figs. 1 and 2) (*15, 16*). Therefore, alloying generally requires extreme conditions such as high temperature and/or pressure in a controlled manner (*17, 18*). Approaches employed toward the synthesis of HMNs include carbothermal shock (*19, 20*), high-temperature migration (*21*), movable type printing (*22*), laser scanning ablation (*23*), plasma treatment (*24*), and wet synthesis (*25, 26*) (Supplementary Table 3). However, these approaches are energy-intensive and require complex equipment, and only a few studies (*17, 27, 28*) have extended the compositional space to systems with more than 10 metals (up to 22 metals incorporated to date (*28, 29*)) (Supplementary Data 1). Furthermore, incorporating HMNs into sub-100 nm carriers in a single step is challenging despite the scientific and technological potential of the resulting materials (e.g., improved stability and processibility, tailorable interfacial properties for advanced catalysis) (*19*). Therefore, the development of a facile approach to regulate metal composition and integration into nanocarriers would expand the library of high-entropy nanomaterials with unique and tunable properties.

Burning hydrocarbon fuel (e.g., candle wax) doped with mixed metal precursors generates a stable source of precursors and simultaneously allows for the continuous homogeneous alloying and strong bonding of immiscible metal species in sub-50 nm uniform metal-containing carbon soot nanoparticles (NPs) via dynamic trapping that resembles that of a flow bed (Supplementary Fig. 3), in contrast to the reported kinetic trapping of carbothermal shock (*19, 20*). Unlike traditional flame combustion (*29–32*), where specialized flame reactors and setups are generally required to generate high temperatures and quench metal precursors into aerosols, the candle flame approach simply involves the ignition of a candle where metal precursors migrate with the paraffin wax along the wick due to capillary action. Specifically, the continuous movement and flow dynamics of the candle flame enable the precursors to travel in a similar manner from the core to the outer flame zone—a dynamic pyrolysis process that differs largely from conventional static pyrolysis (*19*). Herein, we aim to apply a simple candle flame synthesis method to produce compositionally tailorable HMNs at ambient conditions, where the flame naturally outputs a stable and wide temperature gradient from the center of the flame (~1800 K) to the ambient condition of the stainless steel collector (Fig. 1). In addition, we explore the use of HMNs in the electrosynthesis of hydrogen peroxide ($H_2O_2$).

## Results

**Flame synthesis.** To explore the feasibility of flame synthesis, we first examined the candle burning process and the physiochemical properties of the generated soot NPs (Fig. 1a and Supplementary Fig. 3). A stainless steel plate was used as the collector and placed ~20 mm away from a burning wick, where a maximal temperature of ~1800 K was maintained (Fig. 1b). The resulting soot NPs were generally ~40 nm in diameter and featured an onion-like layered structure (Fig. 1c), a high degree of graphitization (>60%; Supplementary Table 4), a large specific surface area (225 $m^2$ $g^{-1}$), and a low resistance (56 Ω) (Supplementary Fig. 4). The soot NPs can be fine-tuned by changing local thermochemical and/or oxidation environments (e.g., collection at inner, outer, or post flames) (Supplementary Figs. 5–7). These properties and tunability make soot NPs promising for many catalytic reactions, particularly when catalytic metal species (e.g., metallic single atoms (SAs) and NPs) are introduced into candle soot-based NPs. Notably, our flame method enables continuous, scalable, and tunable synthesis of high-entropy metal-containing nanomaterials (HMNs), which is significantly different from conventional static pyrolysis (Fig. 1d and Supplementary Table 3). Specifically, the flame temperature naturally surpasses the melting points of most metal precursors (Supplementary Tables 1 and 2), and the high-temperature process is continuous, thereby affording a robust platform for the engineering of diverse metal-containing nanomaterials, including HMNs containing 25 metals (Fig. 1e and Supplementary Data 1).

A characteristic of candle flames is the intrinsically high temperatures spanning from the core to the outer flame (Supplementary Figs. 8 and 9). Uneven temperatures that are commonly found in static pyrolysis typically results in varied quality of the final products; however, the temperature gradient enables the candle flame to function as a flow reactor, which allows the reactants to experience similar processes while traveling through the flame (i.e., dynamic nature of flames). Scaling up was readily achieved by changing wick size, candle number, and/or rotating collection, allowing for the gram-scale synthesis of soot NPs (~1 g $h^{-1}$ per candle) (Supplementary Figs. 10–12 and Supplementary Videos 1 and 2). Importantly, the introduction of metal precursors (e.g., cobalt acetylacetonate) in the hydrocarbon fuel (e.g., paraffin wax) had negligible influence on the resulting peak flame temperatures (~1800 K) even at high metal precursor contents (e.g., 33.3 wt.%) and the supporting soot NPs (Supplementary Figs. 13–16). The sustained temperature was mainly due to the constant high combustion heat generated from candle burning (e.g., $>10^5$ J $g^{-1}$) (Supplementary Fig. 17). The flame synthesis also allows for the use of other fuels with high energy densities, such as kerosene, gasoline, and graphite powder, for the synthesis of soot NPs (Supplementary Figs. 18 and 19 and Supplementary Video 3) (*33*).

**Engineering of SAs and NPs.** We subsequently examined the states of the metallic species in the soot NPs, using cobalt acetylacetonate as a model additive. Well-dispersed single atoms (SAs) of cobalt (Co SAs), Co NPs, and their mixture were observed using aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) for low (<1 wt.%), high (>5 wt.%), and intermediate (1–5 wt.%) cobalt feed concentrations, respectively (Fig. 2a–c). This was preliminarily confirmed by X-ray diffraction (XRD), where Co NPs were likely composed of Co and/or CoO (Fig. 2d) and further supported by X-ray absorption spectroscopy (XAS) using CoO and Co foil as standards (Fig. 2e–h, Supplementary Fig. 20, and Supplementary Table 5). In Co SAs, the Co atom was primarily bound to oxygen, whereas in Co NPs metallic Co–Co bonds were largely found (i.e., ~90%) with a small portion of Co–O observed (~10%). Parameters that influence the size of the metallic NPs include the feed concentration, metal precursor type/number, collector location, rotating collection, and active cooling (Supplementary Figs. 21–24). Specifically, the metallic NPs displayed good homogeneity (e.g., a narrow size distribution of 5.6 ± 1.0 nm (Supplementary Fig. 25) and negligible changes in crystallinity of the metal–soot system; Supplementary Fig. 16), which was independent of the spatial temperature distribution at given conditions (e.g., placing the collector at the outer flame). In general, flame burning with mixed metal precursors could considerably concentrate the metal species in the soot NPs, where the final metal concentration could reach up to ~40 wt.% when its initial content was only ~8 wt.% in the feed (i.e., 1:2 w/w cobalt acetylacetonate/paraffin wax) (Fig. 2i).

**High-entropy SAs.** Flame synthesis could also allow for the incorporation of multiple metals when doped into the hydrocarbon fuel. Importantly, the metal precursors displayed good compatibility with the wax matrix even when nine types of metal acetylacetonates were added simultaneously (Supplementary Fig. 26). We further investigated the metallic states after candle burning, using a quinary metal system (equimolar of Fe, Co, Ni, Cu, and Pd with an overall concentration of 0.16 M) as an example (Fig. 3). High-resolution STEM image showed that metal atoms were embedded within a soot NP (Fig. 3a). Elemental mapping at a larger scale indicated the uniform distribution of these metallic atoms associated with the soot NPs (Fig. 3b). XAS results of the quinary metallic system further confirmed that the state of these metal sites was largely SAs (Fig. 3c,d and Supplementary Figs. 27 and 28). These results thus suggest the capability of our flame method in the synthesis of HMNs where multi-metal components coexist in a high-entropy manner.

**High-entropy NPs.** It is noted that the transition from high-entropy SAs to NPs (when multiple metals coexisted) was also observed simply by changing the total metal content (Supplementary Figs. 29–33). The experimental compositions, as determined by inductively coupled plasma-optical emission spectrometry, agreed well with the STEM data (Supplementary Fig. 34 and Supplementary Table 7). Through this metal incorporation approach, 25 dissimilar metals (Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Sr, Zr, Mo, Ru, Rh, Pd, Cd, In, Sn, Hf, Ir, Pt, Ce, and Nd) were successfully incorporated into a single soot NP in an ultrahigh-entropy pathway (Fig. 4a and Supplementary Fig. 35). The successful formation of HMNs containing 25 metals suggests that our flame synthesis method can avoid phase-separated heterostructures among immiscible elements, leading to an increase in the configurational entropy of mixing ($\Delta S_{\mathrm{mix}}$) (Fig. 4b and Supplementary Fig. 36). Of note, these metal substances display substantially different physicochemical properties (e.g., varied crystal structures (*34*) and melting temperatures (300–2000 K) that typically prevent the formation of homogeneous mixtures (Supplementary Fig. 37 and Supplementary Tables 1 and 2). Specifically, our flame approach also enables uniform mixing of high-valence (e.g., Cr) and refractory (e.g., Mo) metals (Supplementary Fig. 38). Therefore, it is expected that the toolbox of HMNs can be further extended, to at least up to ~50 metals, with the use of appropriate metal precursors.

The structure of the pristine metal-containing NPs could be easily regulated post-synthesis. For example, pyrolysis in 1:10 v/v $H_2$/argon at 350 °C for 2 h led to a change from metal oxide(s) to metal substance/alloys (*17, 35*), as demonstrated by a reduction in the number of metal–oxygen bonds, an increase in oxygen vacancies, and a reduction in metallic valence (Supplementary Fig. 39). To further demonstrate these changes, we investigated the aforementioned 9-metal system ($\Delta S_{\mathrm{mix}} = 13.4$ J mol$^{-1}$ K$^{-1}$) (Fig. 4c–g). Upon reduction, the pristine high-entropy oxides (HEO-9) were transformed into high-entropy alloys (HEA-9) as evident by the down shift (~1°) of the XRD peak, owing to oxygen consumption-induced compressive strain and volume shrinkage (Fig. 4c) (*36, 37*). A decrease in the inter-lattice spacing was also observed (by ~0.05 Å) by STEM, whereas the crystal structure was largely unchanged (i.e., face-centered cubic (FCC) system) (Fig. 4d,e and Supplementary Figs. 40 and 41). These changes were visualized by elemental mapping, for example, the disappearance of oxygen within the HEA-9 NPs (Fig. 4f,g). Notably, HEOs can also be converted in to HEAs by wet reduction in $NaBH_4$ solution without the generation of apparent byproducts (e.g., boron species), thus providing a protype of continuous production of soot-based HEAs (Supplementary Figs. 42–44) (*38, 39*). In addition to preparing NPs with a typical soot–metal oxide chemistry, a series of HMNs were obtained with different chemistries (e.g., sulfides, phosphides, and fluorides) simply by flame synthesis with either doped organic chemicals (Supplementary Figs. 45–47), metallic species (e.g., chlorides, nitrates, and acetates) (Supplementary Figs. 48–51), by using diverse substrates (Supplementary Fig. 52) or carbon-free metals (Supplementary Fig. 53). Furthermore, additional control parameters, including rotating collection (Supplementary Fig. 19 and Supplementary Video 2) and active cooling (Supplementary Figs. 23 and 54), can be used to improve the homogeneity and quality of the products. We note that the metal composition in the final HMNs is slightly different from the starting feed materials, likely due to vapor losses at high temperatures as the precursors have varied physicochemical properties (e.g., vapor pressure) (Supplementary Fig. 55). With this understanding, a precursor–compensation approach was adopted to fine-tune the metal composition and size, allowing for the engineering of sub-5 nm HMNs with close-to-identical concentrations of different metals (Supplementary Figs. 56–58 and Supplementary Table 8), thereby providing a versatile platform for advanced electrochemical applications.

**Molecular dynamics (MD) simulations.** Reactive MD simulations were conducted to study the formation of metal–soot NPs (*40*). The simulation was constructed using metal ions and coronene (a typical polycyclic aromatic hydrocarbon (PAH) assumed to be a building block of soot), as the reactive intermediaries (Supplementary Fig. 59), and was performed in NPT ensemble (constant number, pressure, and temperature) using the large-scale atomic/molecular massively parallel simulator (LAMMPS) software package (*33, 41-43*). Coronene molecules and metal ions exhibit association, clustering, and growth of soot and/or metal NPs at different stages (*44, 45*). These could be observed at different temperatures though the clustering rates were different (Fig. 5a–d and Supplementary Fig. 60). Generally, high temperatures (e.g., >1000 K) stabilized the coronene molecules, whereas low temperatures (e.g., <1000 K) were favorable for rapid formation of soot NPs (Supplementary Fig. 61 and Supplementary Videos 4 and 5) (*46*). When the metal ions were present (e.g., Fe), clustering was either delayed at low temperatures or accelerated at high temperatures owing to different clustering pathways. Low temperatures resulted in non-reactive metal–coronene association, whereas high temperatures resulted in the production of more reactive carbon species, as catalyzed by the metals (by releasing small molecules), which therefore expedited their aggregation with the metal ions/NPs (Supplementary Fig. 62). In addition, we observed that the initial metal concentration is key to determining the final states of metals (i.e., SAs or NPs) (Fig. 5e and Supplementary Fig. 63). For example, in the cobalt–soot system (1000 K), the radial distribution function profiles of Co–Co distance suggest that metals tend to cluster and form NPs at high concentrations (e.g., >5 wt.%; Supplementary Video 6) and SAs can be retained at low cobalt concentrations (e.g., 2 wt.%; Supplementary Video 7). This was supported by the presence/absence of the peaks at 2.37 Å (dimers) or ~4–6 Å (trimers or larger ones). These results are also consistent with those observed for multimetal systems (e.g., Co, Ni, Cu, Zr, and Pt) (Fig. 5f). Moreover, the predominant peak at ~2 Å of the metal–carbon radial distribution functions suggests strong metal–support interactions, possibly useful for engineering robust catalysts (Supplementary Fig. 64). These MD simulations, though qualitative and simplified compared to the actual flames, suggest the possible clustering pathways as well as the capability of candle burning in producing SAs or NPs particularly of high-entropy nanomaterials.

**Application of HMNs.** Next, we investigated the potential application of our HMNs in the production of $H_2O_2$, which is an important chemical with a growing global market (e.g., as an oxidizer and monopropellant in chemical production, rocketry, and health fields). As a proof-of-concept, a quinary (i.e., Fe, Co, Ni, Cu, and Pd) high-entropy alloy nanomaterial (HEA-5) was carefully designed (via analytical investigation, experimental validation, and theoretical calculations; Supplementary Figs. 65–68) and prepared using our method and compared with its high-entropy oxide counterpart (HEO-5) in electrochemical oxygen reduction reaction (ORR) (Supplementary Fig. 69). Of note, although applicable in non-alkaline conditions, our HEA-5 catalyst showed the best performance in alkaline conditions (Supplementary Fig. 70) with negligible $H_2O_2$ degradation (Supplementary Fig. 71). A rotating ring-disc electrode in a three-electrode cell was employed using an alkaline electrolyte (0.1 M KOH) to obtain the characteristic polarization curves—HEA-5 exhibited a higher $H_2O_2$ selectivity (>99% at ~0.60 V and >95% over a wide potential range of 0.4–0.7 V) and faster ORR kinetics (e.g., a low Tafel slope of 53 mV dec$^{-1}$) than HEO-5. No apparent decay in the activity, selectivity, or Faradaic efficiency (~100%) was observed for HEA-5 even after >150 h of chronoamperometry testing (at an applied potential of −0.236 V) (Supplementary Figs. 72 and 73). The long-term stability is likely due to the intrinsic carbon coating on the HEA-5 surface (Supplementary Figs. 74–77). A high $H_2O_2$ production rate (1170 mmol $g_{cat}^{-1}$ h$^{-1}$ at 10 mA cm$^{-2}$) was obtained when a H-shaped electrolyte cell was used (Supplementary Fig. 78). Moreover, HEA-5 demonstrated an industrial current density of 300 mA cm$^{-2}$ at an overpotential of 295 mV using a customized flow cell (1.0 M KOH) (Supplementary Figs. 79 and 80). To maintain this current density, a two-electrode full-cell voltage of 2.72 V was required, and negligible change (<0.4%) was observed even after >120 h ORR, indicating the high stability of the HEA-5-based cell (Supplementary Figs. 79 and 81). A consistent concentration of $H_2O_2$ of ~6.1 wt.% was attained for HEA-5 (compared with ~4.3 wt.% for our HEO-5, <0.5 wt.% for a commercial Pd/C benchmark, and <5 wt.% generally achieved in the literature), with a Faradaic efficiency of >95% toward $H_2O_2$ (Supplementary Figs. 79, 82, and 83 and Supplementary Table 9). A techno-economic analysis (TEA) was then performed through theoretical analysis and Aspen Plus simulations (Supplementary Figs. 79 and 84–95, Supplementary Tables 10–15, and Supplementary Data 2). Specifically, the electrosynthesis approach using HEA-5 outperformed the conventional anthraquinone oxidation method to achieve the same $H_2O_2$ concentration (Supplementary Fig. 95). The TEA report therefore highlights the promising industrial application of this class of HNMs and their potential in the $H_2O_2$ production market.

Hydrocarbon burning with naturally high temperatures not only serves as a robust and versatile platform for novel materials design and discovery but also holds promise in advanced self-cleaning (Supplementary Fig. 96 and Supplementary Videos 8 and 9) and many other advanced catalytic applications such as carbon dioxide reduction (Supplementary Fig. 97) and photothermal conversion of organic molecules (Supplementary Fig. 98). The ease of control, relatively low cost, and potential to tailor composition open avenues for possible scientific and industrial breakthroughs.

## Discussion

Varying the metal composition and concentration, as well as the inclusion of organic dopants generates a library of HMNs (metallic SAs, alloy oxide NPs, and heteroatom-doped metal–soot NPs) containing up to 25 dissimilar metallic elements. The HMNs synthesized by this method have tunable sizes (from SAs to metallic NPs) and are uniformly dispersed across nanoscale onion-like soot nanostructures (30–50 nm) with tunable wettability (from liquid pinning to rolling). The compositional flexibility and easy-to-operate experimental setup enable the precise design of high-performance electrocatalysts with enhanced activity and structural stability for industrial processes (e.g., $H_2O_2$ production). Reactive MD simulations suggest that the natural temperature gradient is essential for alloy NP formation (i.e., via reactive association and clustering), where the decomposed metallic precursors and PAHs undergo association, followed by PAH stacking and soot clustering, and finally metallic alloy fusion into clusters and NPs within the soot nanostructures. This flame synthesis technique has numerous features: it can realize high temperatures without external energy input; it operates in open air; it enables material composition customization; it is versatile in terms of the wide range of precursors that can be used; and it has potential for scientific and industrial applications. Our approach therefore provides a versatile platform for multicomponent design, largely expanding the toolbox of HMNs and their potential for diverse applications such as self-cleaning, electroreduction of oxygen/carbon dioxide, and photothermal conversion of organics.

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**Author contributions:** S.P. conceived the idea (with the assistance of Z.L. and R.G.), designed, and led the project. All authors performed research and/or analyzed data with intellectual contributions. S.P., F.C., and Z.L. drafted the manuscript with input from all authors. All authors have given approval to the final version of the manuscript.

**Competing interests:** The authors declare no competing interests.

**Figure Captions:**

**Fig. 1 | Flame synthesis of metal-containing nanomaterials. a**, Scheme illustrating the burning of paraffin wax with metal acetylacetonates as the dopants. **b**, Soot collection and infrared thermal imaging of a typical flame synthesis setup. The temperature of the outer flame (white circled area) is ~1800 K. **c**, Scanning electron microscopy (left) and TEM (right) images of candle soot NPs. **d**, Comparison of different synthesis methods in terms of temperature and time. Shading indicates the temperature range of our flame synthesis method. See Supplementary Table 3 for more details. **e**, Histogram of research to date in the synthesis of metal-containing nanomaterials, where the preparation of metal-containing nanomaterials with more than eight metals is largely unexplored. The sources of the datasets (405 in total) are included in Supplementary Data 1 (data accessed February 2025).

**Fig. 2 | Transition from SAs to NPs. a–c**, Typical high-resolution HAADF-STEM images (left) and corresponding fast Fourier transform (FFT) patterns (right) of the metal species in cobalt–soot systems prepared at varying metal concentrations (~1, ~3, and ~5 wt.%, respectively). **d**, XRD patterns of Co SAs and NPs. **e**,**f**, K-edge X-ray absorption near edge structure spectra (**e**) and Fourier transform K-edge extended X-ray absorption fine structure spectra (**f**) of Co SAs, Co NPs, CoO, and Co foil. **g**,**h**, Wavelet transform analysis of Co SAs (**g**) and NPs (**h**). **i**, Concentration of Co in the feed and resulting soot.

**Fig. 3 | High-entropy SAs (Fe, Co, Ni, Cu, and Pd) supported by soot NPs. a**, High-resolution STEM image of a soot NP featuring sites of single metal atoms. The arrows indicate part of the single metal sites. The metal precursors are equimolar in the molten wax with an overall metal concentration of 0.16 M. **b**, HAADF-STEM image and elemental mapping of aggregated soot NPs supporting single metal atoms. **c**,**d**, XANES spectra (**c**) and EXAFS fittings (**d**) for individual metals (K-edge) in the quinary metal system. Metal foils are shown for reference. See Supplementary Fig. 27 and Supplementary Table 6 for fitting details.

**Fig. 4 | Flame synthesis of a HMN library. a**, Toolbox of metal acetylacetonates: orange, 25 metals studied in this work; blue, nonmetallic elements involved in this work; pink, commercially available but not studied. **b**, Theoretical (i.e., isometric ratio) and experimental mixing entropy of metals. Shadings indicate relevant regions of low, medium, high, and ultrahigh entropies. **c**, XRD patterns of two nonary high-entropy systems ($Fe_{0.09}Co_{0.12}Ni_{0.12}Cu_{0.05}Ru_{0.15}Rh_{0.11}Pd_{0.11}Ir_{0.09}Pt_{0.16}$): HEO-9 (prepared by direct candle burning, i.e., metal oxides) and HEA-9 (obtained after reduction of HEO-9, i.e., metal alloys). **d**,**e**, High-resolution HAADF-STEM image (**d**) and corresponding FFT pattern (**e**) of HEO-9. An FCC phase structure with twin boundaries is shown. **f**,**g**, Elemental imaging showing the change in the chemistry of HEO-9 (**f**) into HEA-9 (**g**). Scale bars are 5 nm for all images.

**Fig. 5 | Metal–soot clustering simulations. a–c**, Series of representative images of the simulated cell studies in this work, showing the initial configuration (0 ns) and the evolutions (0.1 and 0.3 ns) of metal–soot clustering at 700 and 1000 K. The simulated cell is constructed using 200 coronene molecules (grey disk) and 400 cobalt ions (red), corresponding to a high concentration of cobalt (~30 wt.%). **d**, Number of clusters throughout the simulated reaction time frame (1 ns). Shading indicates the difference. **e**, Radial distribution functions (1000 K) of Co–Co distance as a function of different amounts of metals included. **f**, Radial distribution functions of metal-to-metal distance when multiple metals are included (Co, Ni, Cu, Zr, Pt) at either low or high metal concentrations, simulating the high-entropy systems (HE SAs and NPs). Shadings in **e** and **f** indicate regions of interest.

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## Methods:

**Premixing of precursors.** Metal acetylacetonates were mainly used in this work and mixed with paraffin wax to prepare candle precursor solutions. Metal acetylacetonates were first dissolved in tetrahydrofuran (minimal volume as long as the metal precursors were fully dissolved) separately or mixed in tetrahydrofuran solution, depending on how many types of metals were combined. The prepared solution was added dropwise to the molten paraffin wax at 100 °C under stirring and further heated for 30 min to evaporate the solvent. The final molar concentration of the total metal elements in the molten paraffin wax was in the range of 0–1.56 M (Fig. 2i), depending on whether metallic SAs or NPs were prepared. Typically, for the synthesis of SAs, the total metal molar concentration in the feed was 0.16 M (e.g., 1.1 wt.% Co in Fig. 2a). For the synthesis of NPs, the overall molar concentration of metals in feed was 0.94 M (e.g., Fig. 2c and Fig. 4b). Specifically, the corresponding metal weight fraction of the unary Co system as shown in Fig. 2c was 5.3 wt.%. When more than one metal precursor were involved (e.g., 5-, 9-, 11-, and 25-metal systems as shown in Fig. 4b), the individual metal molar concentrations in the feed were identical. A cotton thread (24 strands) was inserted in the fully mixed molten precursor, which was naturally cooled to room temperature (i.e., 20–25 °C) in a customized cylindrical mold made of polymethyl methacrylate (diameter = 2 cm) to obtain a candle that was used subsequently. The same mixing protocol was used when other metal salts were used.

**Candle burning and soot collection.** The prepared candle was ignited, and a stainless steel collector was placed ~20 mm above the wick (i.e., outer flame). Collection at the inner flame was performed at ~10 mm above the wick. Collection was also performed using pre-cooled or pre-heated collectors. Preheating was achieved using a laboratory oven at ~170 °C. To achieve active cooling, a cooling system was used to achieve −40 °C. The system, which consists of a semiconductor controller (TLTP-TEC2415, 450 × 133 × 350 mm) and a cooling stage (200 × 100 × 50 mm), was supplied by Wuhan Zhongqi Optoelectronic Technology Co. Ltd. Unless specified otherwise, this work focused on the collection of (metal-containing) soot NPs at the outer flame without active cooling. *Caution, fire and smoke! Use appropriate personal protective equipment (e.g., gloves, googles, and facial mask) and operate in fume hood.* The candle soot-based samples were collected using a stainless steel blade for subsequent use. The candle burning approach was altered by using a different (1) number strands of cotton thread as the candle wick (24 strands unless specified otherwise), (2) length of candle wick (1 cm unless specified otherwise), and (3) candle diameter (2 cm unless specified otherwise), and by varying (4) the mobility of the collector (still unless specified otherwise) and (5) the type, number, and concentration of metal precursors. Five systems of HEOs supported by carbon soot NPs were synthesized in this work using the candle burning approach i.e., HEO-5 (Fe, Co, Ni, Cu, and Pd; our focus), Sub-5 nm HEO-5 (Ru, Rh, Pd, Ir, and Pt; only for demonstrating sub-5 nm NPs), HEO-9 (Fe, Co, Ni, Cu, Ru, Rh, Pd, Ir, and Pt), HEO-11 (Fe, Co, Ni, Cu, Zr, Ru, Rh, Pd, Ir, Pt, and Ce), and HEO-25 (Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Sr, Zr, Mo, Ru, Rh, Pd, Cd, In, Sn, Hf, Ir, Pt, Ce, and Nd). Equimolar metal acetylacetonates as the metal precursors with an overall metal concentration in the molten precursor of 0.94 M were used.

**Flame temperatures.** To determine the temperature of the candle flame, we used an infrared thermal camera (PT850, installed with high temperature lens with an operating range of −40–2500 °C). The camera was equipped with a vanadium oxide microbolometer detector (7.5–14 μm), generating high-resolution thermal images up to 1280 × 1024 pixels. The distance to the flame during measurement was 0.7 m and data accuracy was ±10 K. During operation of the instrument, its imaging system scans and detects target objects sequentially from left to right and from top to bottom, decomposes the target objects into pixels one at a time, converts the radiant energy through the infrared detector, and generates the signal current corresponding to the change in the radiant energy of the flame. The temperatures are finally displayed digitally in color, which are analyzed using the ThermoTools Infrared Analysis software.

**Flame synthesis mechanism.** Burning candles can generate high temperatures as well as a large temperature gradient both along and normal to the flame direction. The local high temperature allows for the evaporation/decomposition/reaction of wax molecules (long-chain alkanes) and metal precursors, facilitating the formation of soot clusters and their growth by sintering and coalescence (*47*). The temperature gradient in the precinct of the flame enables the condensation and collection of soot NPs at the collector (*48*). Specifically, the vaporized/decomposed metal precursors can bind to reactive oxygen/carbon species within the flame, largely forming gaseous/liquid metal oxides that undergo condensation, nucleation, and solidification at the soot NP support. Of note, for the synthesis of HEOs, the high flame temperature (~1800 K) likely plays an essential role. At this temperature, most of the metal precursors can vaporize, allowing for the fusion of diverse metals into a single NP in a high-entropy way.

**Conversion of HEOs into HEAs.** *Dry method.* The HEOs can be converted into HEAs by thermal pyrolysis with hydrogen. Briefly, the soot-based HEO sample (50 mg) was placed in a tube furnace (length = 1 m, diameter = 50 mm) and flushed with a stream of argon/hydrogen mixture (10:1 v/v; 100 mL $min^{-1}$) for 20 min. The temperature was then increased to 350 °C at a rate of 2 °C $min^{-1}$ and maintained for 2 h. The HEAs were obtained after cooling to room temperature (i.e., 20–25 °C). A possible mechanism of this dry method can be described by these two reactions as follows (*49, 50*): $xH_2 + MO_x \rightarrow M + xH_2O$ (g) and $xC + MO_x \rightarrow M + xCO$ (g). Unless specified otherwise, this dry method was mainly used to convert HEOs into HEAs (e.g., HEA-9 in Fig. 4, HEA-5 in Supplementary Fig. 79). This approach was also applicable to other metal-doped soot systems such as Co-doped soot nanomaterials in Supplementary Fig. 39. *Wet method.* $NaBH_4$ in water was used as the reducing agent. Briefly, $NaBH_4$ (50 mg) and the HEO sample (50 mg) were added to water (150 mL) in a round bottom flask. The mixture was magnetically stirred at 50 °C for 10 min. The suspension was separated by filtration and rinsed with copious amounts of water. HEAs were obtained after drying in a vacuum oven at 50 °C for 24 h. This method was studied for demonstration purposes only and the relevant data are mainly shown in Supplementary Figs. 38 and 42.

**Reactive MD simulations.** Reactive MD simulations were conducted to explore the formation of soot clusters in the presence or absence of metallic atoms. Coronene molecules were used as building blocks of the soot NPs. Within a cubic simulation domain, 200 coronene molecules were distributed randomly, and metallic atoms were introduced at varying concentrations and an initial density of 0.05 g $cm^{-3}$ using the Materials and Processes Simulations (MAPS) 4.4 platform [Scienomics, MAPS®, Paris, 2015]. Specifically, soot formation was investigated using coronene as the carbon source in the presence of 0–30 wt.%

metals for single metal systems, including Co and Fe ranging between 700 and 1600 K. Additionally, soot formation in the presence of 5-metal systems was explored, encompassing 3.7 and 38.4 wt.% of equimolar Co/Ni/Cu/Zr/Pt at 700 and 1000 K. All systems were simulated in the NVT ensemble (constant number of atoms, volume, and temperature) on LAMMPS (*51*) with periodic boundary conditions implemented in all three directions with an integration timestep of 0.25 fs. The ReaxFF forcefield of Nielson et al. (*52*) was employed for the coronene/Co/Ni/Cu/Zr/Pt interactions, whereas the forcefield of Islam et al. (*53*) was employed to model the coronene/Fe interactions.

**Configurational entropy of mixing.** The configurational entropy per mole of our HMNs can be calculated based Boltzmann's hypothesis (*54, 55*) on the relationship between the entropy and the complexion of a system:

$\Delta S_{\text{mix}} = -R\sum x_i \ln x_i$ (Eq. 1)

where $R$ is the gas constant (8.314 J $K^{-1}$ $mol^{-1}$) and $x_i$ is the mole fraction of the $i^{\text{th}}$ element. In an equiatomic alloy, $x_1 = x_2 = x_3 = x_i = x_n$, and the mixing entropy is maximal:

$\Delta S_{\text{mix}} = -R\ln\frac{1}{n} = R\ln n$ (Eq. 2)

where $n$ is the number of elements in the alloy. Therefore, the configurational entropy of high-entropy NPs increases with the number of elements. For example, for alloy systems with equimolar elements, $\Delta S_{\text{mix}}$ values are 1.39$R$, 1.61$R$, and 1.79$R$ when $n$ = 4, 5, and 6, respectively.

**$H_2O_2$ electrosynthesis.** To evaluate the catalyst at industrially relevant current densities, electrochemical measurements were performed in a customized flow cell (three-electrode). The flow cell enabled the electrochemical reactions to proceed without the diffusion-limitation of reactant oxygen. A YLS-30T carbon paper with a 20.0 wt.% polytetrafluoroethylene was used as the gas diffusion layer (GDL). The catalyst was air-brushed onto the GDL as the cathode, achieving a load of ~0.25 mg $cm^{-2}$. The catalytically active surface area of the GDL was 1 × 1 $cm^2$, which was in contact with the electrolyte flow compartment. Nickel foam was used as the anode for water oxidation. A 3-mm thick polyetheretherketone spacer with a hole for the reference electrode (Ag/AgCl) was sandwiched between the GDL cathode and the Ni foam anode, forming a three-electrode cell configuration. This flow cell was operated with 1.0 M KOH solution as both the anolyte and catholyte, which were separated by a Nafion 115 membrane (1.5 × 1.5 $cm^2$) between the polyetheretherketone spacer and the anode bipolar plate. The liquid flow rates at the cathode and anode were 5 mL $min^{-1}$, and the cathodic gas flow rate was 40 mL $min^{-1}$. Prior to the test, the electrolyte liquid and oxygen gas were kept flowing for 30 min to achieve a three-phase gas–liquid–solid equilibrium. Linear sweep voltammetry experiments were conducted from 0 to −0.8 V (vs. reversible hydrogen electrode (RHE)) at a scan rate of 10 mV $s^{-1}$. The electrosynthesis of $H_2O_2$ was also evaluated at industrial-relevant conditions using a two-electrode flow cell (similar to the above setup but without a reference electrode). The anode and cathode were circulated with 1.0 M KOH at a flow rate of 3.0 mL $h^{-1}$, which was controlled by a peristaltic pump. An oxygen stream of 40 mL $min^{-1}$ was supplied to the cathode. The flow cell was first stabilized at the relevant working potential for 30 min before collecting the $H_2O_2$ products.

**Characterization.** A spherical aberration-corrected transmission electron microscope equipped with a condenser lens corrector (Themis Z 3.2) was used for the analysis of metallic SAs/NPs and chemical composition. Carbon and oxygen vacancies/defects were evaluated by electron spin resonance spectroscopy using a JEOL JES-FA 200 spectrometer at room temperature (i.e., 20–25 °C). XAS and small-/wide-angle X-ray scattering (SAXS/WAXS) data were collected at the Australian Synchrotron facility, part of the Australian Nuclear Science and Technology Organisation. The samples were investigated using the SAXS/WAXS beamline (using cameras (1700 mm and 900 mm), with Pilatus 1M and 200 K as the detectors, operating at 12 keV in transmission mode). The Scatterbrain, RAW, and McSAS 1.3.1 softwares were used for SAXS/WAXS data analysis. The K-edge X-ray absorption near edge structure spectra and Fourier transform K-edge extended X-ray absorption fine structure (EXAFS) spectra of the samples were obtained using the XAS beamline (in Hutch-B) equipped with monochromator Si(111) at room temperature (i.e., 20–25 °C). An entrance slit with a vertical opening of 1 mm was used. Each spectrum was scanned using a step size of 0.5 eV in the region from −50 eV to +1000 eV at the absorption K-edge. The Athena and Artemis softwares were used for XAS data analysis.

**Data availability:** All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Information. Source data are provided with this paper.

**Code availability:** Codes for molecular dynamics simulations are provided as part of the replication package in the Supplementary Information.

**Methods-only References:**

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