

Revealing High-Temperature Reduction Dynamics of High-Entropy Alloy Nanoparticles via *In Situ* Transmission Electron Microscopy

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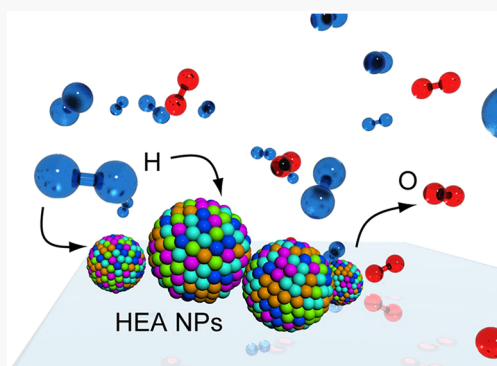
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Supporting Information

ABSTRACT: Understanding the behavior of high-entropy alloy (HEA) materials under hydrogen (H_2) environment is of utmost importance for their promising applications in structural materials, catalysis, and energy-related reactions. Herein, the reduction behavior of oxidized FeCoNiCuPt HEA nanoparticles (NPs) in atmospheric pressure H_2 environment was investigated by *in situ* gas-cell transmission electron microscopy (TEM). The reduction reaction front was maintained at the external surface of the oxide. During reduction, the oxide layer expanded and transformed into porous structures where oxidized Cu was fully reduced to Cu NPs while Fe, Co, and Ni remained in the oxidized form. *In situ* chemical analysis showed that the expansion of the oxide layer resulted from the outward diffusion flux of all transition metals (Fe, Co, Ni, Cu). Revealing the H_2 reduction behavior of HEA NPs facilitates the development of advanced multicomponent alloys for applications targeting H_2 formation and storage, catalytic hydrogenation, and corrosion removal.

KEYWORDS: High-entropy alloys, nanoparticles, *in situ* TEM, reduction, phase segregation



INTRODUCTION

High-entropy alloys (HEAs) have attracted significant attention in recent years.^{1–4} Because of the built-in high entropy effect from the atomically mixed more than five elements, HEAs exhibit unique characteristics in mechanical properties, thermal stability, and oxidation/corrosion resistance.^{2–5} While extensive research efforts have been focused on the fabrication of bulk HEAs through solid-state processing,^{6–8} bulk melting,^{9,10} and additive manufacturing,^{1,11,12} the recent advances in synthesizing single-phase HEA nanoparticles (HEA NPs) have expanded their applications in catalysis, electronics, and energy-related applications. Recently, carbothermal shock,¹³ aerosol,¹⁴ and fast moving bed pyrolysis¹⁵ methods are shown to provide scalable quantities of HEA NPs for large-scale applications with high uniformity of atomic distribution and controllable size ranges.

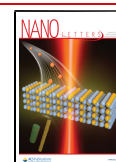
In many potential applications of HEA NPs, the materials are exposed to oxidizing and reducing environments. For instance, as one of the most common reducing agents in chemical reactions, understanding the behavior of HEAs in H_2 environment is key for the future development of advanced materials. To date, HEAs have been investigated for their hydrogen embrittlement,^{16–19} hydrogen storage,^{20,21} hydrogenation,^{22,23} and water splitting properties.²⁴ However, little is known on how HEAs behave in reducing environmental conditions. Currently, several studies on the oxidation of bulk HEAs in air^{25–30} have identified different reaction kinetics including linear and parabolic for various compositions at high temperatures. The

authors recently reported the oxidation of HEA NPs under dried air at 400 °C and showed that Kirkendall effect governed the logarithmic behavior of the oxide layer growth kinetics.³¹ Here, we used *in situ* closed-cell atmospheric pressure transmission electron microscopy^{32–44} to study the high-temperature reduction behavior of oxidized FeCoNiCuPt HEA NPs in H_2 environment. In our study, closed-gas cell design^{37–43,45} based on microfabricated devices was used to expose the NPs to atmospheric pressure H_2 at 400 °C. In order to investigate the local structural and chemical evolution in the NPs, *in situ* high-angle annular dark-field (HAADF), annular bright-field (ABF) imaging, and energy dispersive spectroscopy (EDS) were used. In the H_2 reducing environment, the oxide layer over HEA NPs expanded and transformed to porous structure as H_2 reacted with oxygen. Oxidized Cu was fully reduced to Cu NPs while Fe, Co, and Ni remained in their oxidized form. The H_2 reduction resulted in significant morphological and chemical changes where the core of the NPs reduced in size while the oxide shell was expanded with Cu NPs forming at outermost oxide surfaces.

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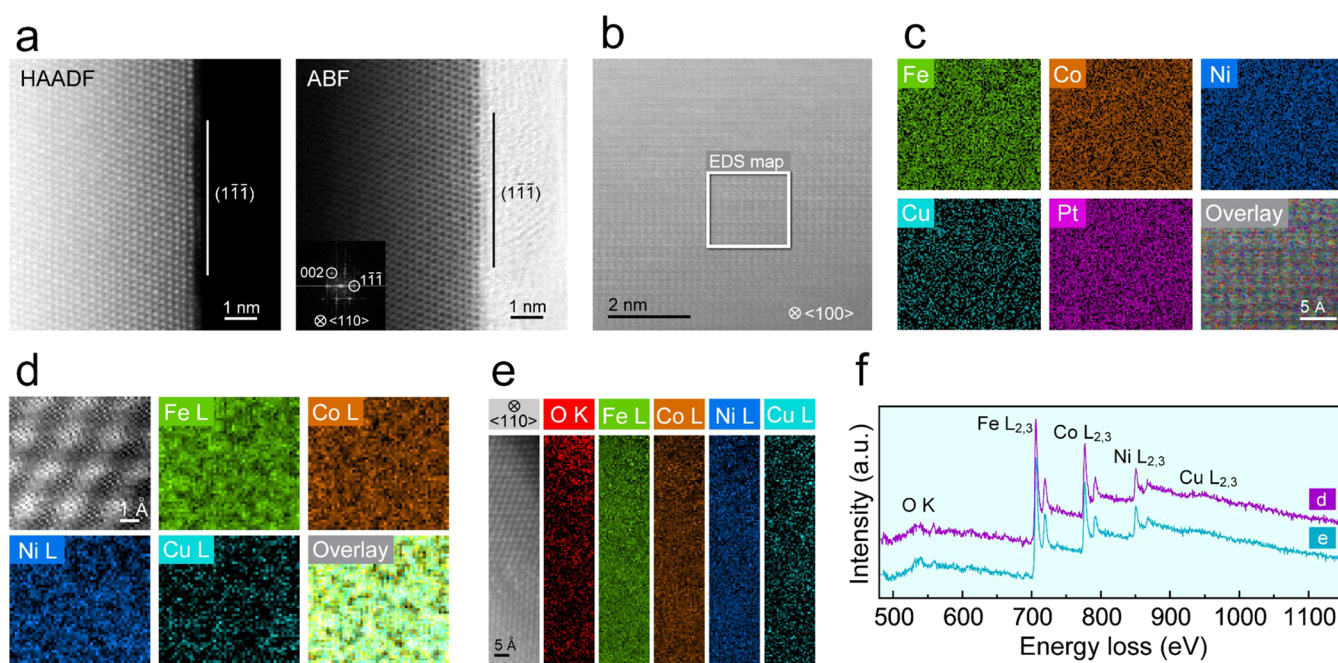


Figure 1. Electron microscopy characterization of HEA NPs on atomic structure and chemical composition. (a) The HAADF and ABF images show the atomic structure of as-prepared HEA in the $\langle 111 \rangle$ zone axis. Inset in ABF image shows the FFT with (111) and (002) planes highlighted. (b) The HAADF image from the $\langle 100 \rangle$ zone axis of HEA NP with the EDS map region highlighted in the box. (c) Atomic resolution EDS maps for boxed region in panel b showing all five elements and the overlaid image. (d) The atomic resolution EELS map showing atoms in the $\langle 110 \rangle$ zone axis and corresponding Fe, Co, Ni, and Cu maps. (e) The EELS map from another region in the $\langle 110 \rangle$ zone axis HEA NP extracted from O K-edge and Fe, Co, Ni, Cu L-edges. (f) The EEL spectra from the region in panels d and e.

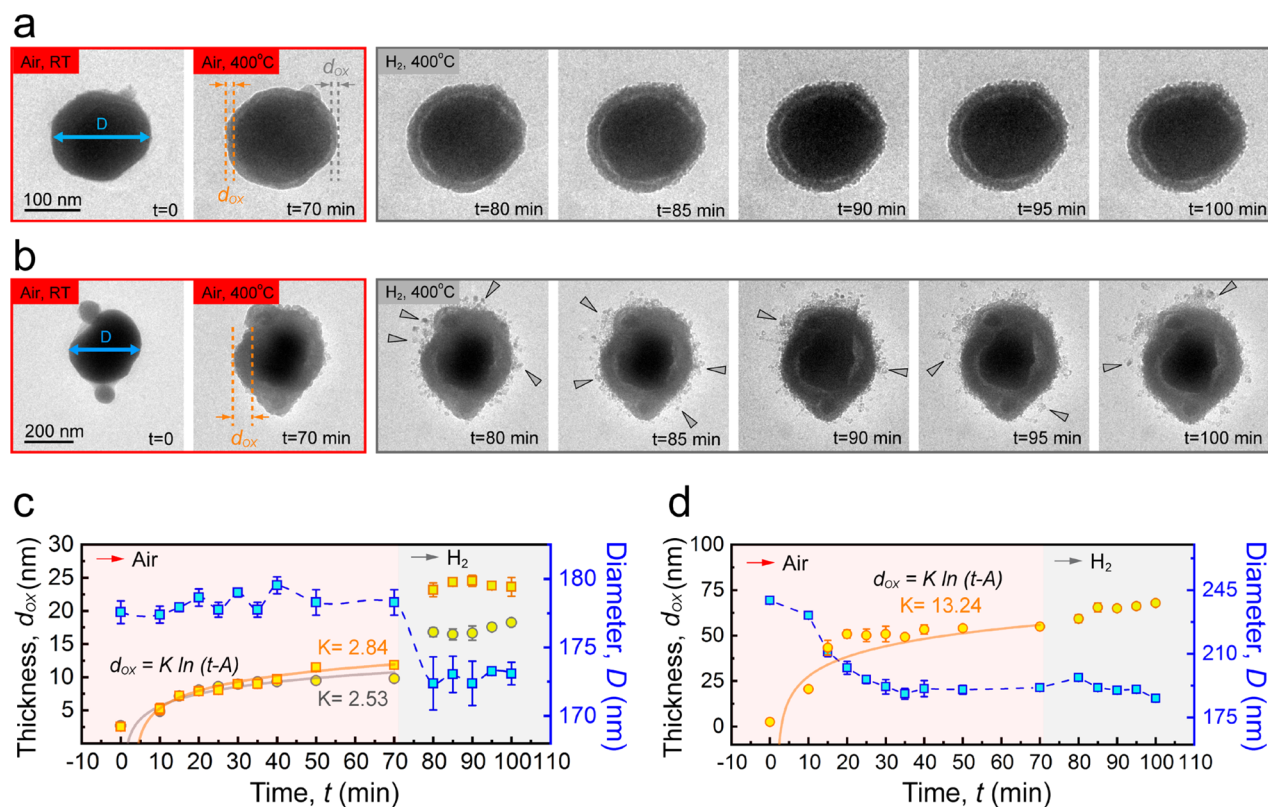


Figure 2. Reduction of oxidized HEA NPs. (a,b) TEM image series of an HEA NP oxidation in air (red box) followed by reduction in H_2 (gray box). The temperature is RT in the first frame and 400 °C in all other frames. (c,d) Evolution of the oxide thickness d_{ox} and HEA NP diameter D during oxidation and reduction. As marked in panels a and b, the diameter D is shown in blue while oxide thickness d_{ox} is shown in orange (and gray) in left (and right) directions.

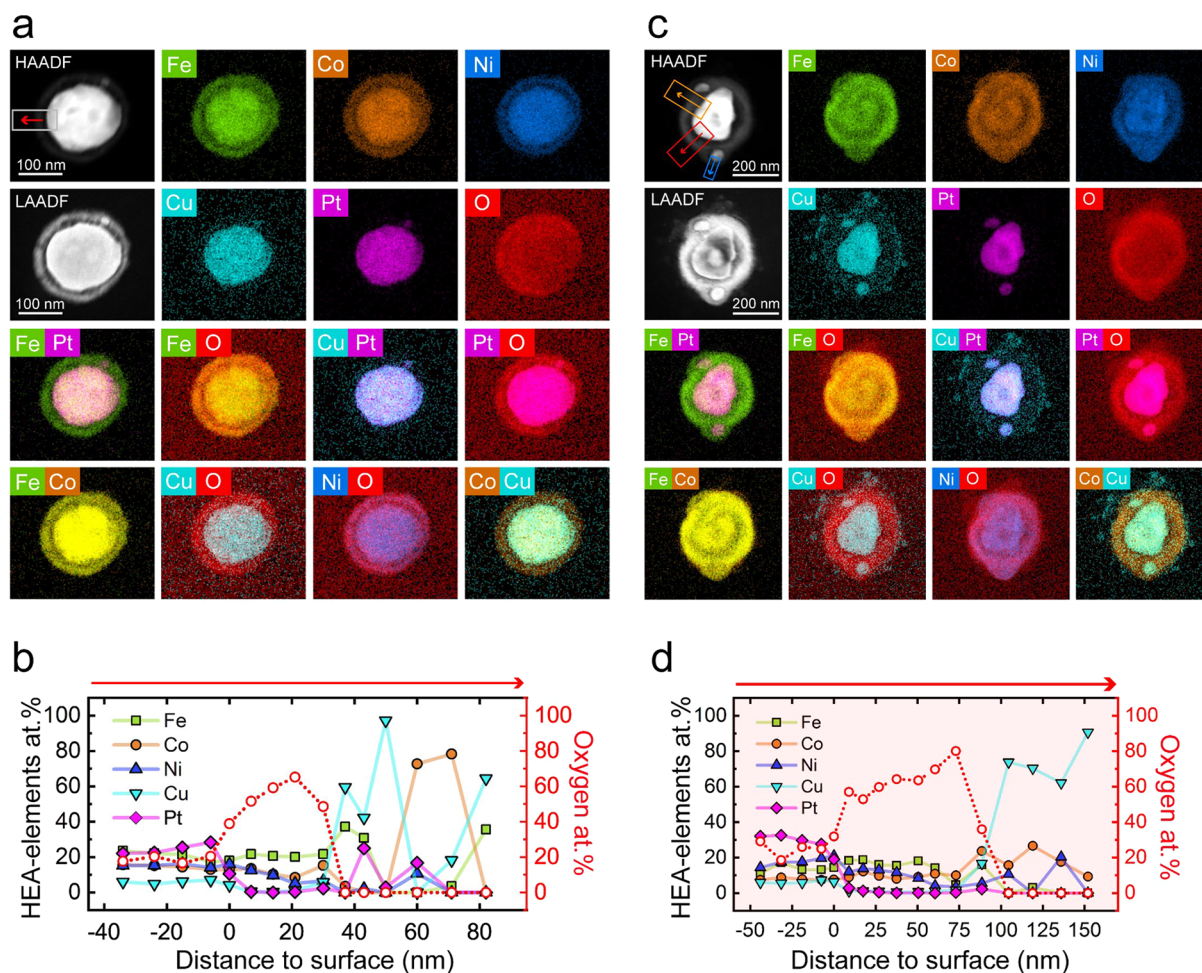


Figure 3. STEM-EDS of HEA NPs collected after *in situ* reduction. (a,c) STEM (HAADF and LAADF) images of HEA NP shown in Figure 2a,b, EDS maps of metal elements and O as well as selected overlaid EDS maps. (b,d) Atomic percentage distribution of metal elements and O. The arrows point to the directions in the same manner as marked in the HAADF image in panels a and c.

RESULTS

The morphology and composition of the synthesized HEA NPs were characterized by X-ray powder diffraction (XRD), SEM, and TEM in our previous work,^{14,31} where the average composition was shown to be $\text{Fe}_{0.28}\text{Co}_{0.21}\text{Ni}_{0.20}\text{Cu}_{0.08}\text{Pt}_{0.23}$ for all size ranges. Here, we provide additional atomic resolution STEM imaging combined with STEM-EDS and STEM-electron energy loss spectrum (EELS) to confirm the chemical homogeneity at the atomic level. Figure 1a shows HAADF and ABF images of HEA NP along $\langle 110 \rangle$ zone axis in a face-centered cubic (fcc) crystal structure. Atomic resolution STEM-EDS maps from the $\langle 100 \rangle$ zone axis of an NP (Figure 1b) shown in Figure 1c suggest homogeneous mixing of the five elements. In addition, atomic resolution STEM-EELS maps (Figure 1d) on an NP in the $\langle 110 \rangle$ zone axis further confirm the homogeneous distribution. Although the contrast of native oxide in the STEM images is not very obvious, the O K-edge map in Figure 1e shows more oxygen presence closer to the particle surface originating from the native oxide. The EEL spectra from regions in Figure 1d,e are then extracted and compared in Figure 1f. The two spectra are almost identical showing the O K-edge and $L_{2,3}$ -edges from transition metals, confirming the homogeneity in elemental distribution.

Next, *in situ* reduction on the HEA NPs was performed in TEM. First, a reduction step was carried out directly on the

pristine HEA NPs, but this resulted in no appreciable changes in the surface structures (Figure S1a,b). Hybrid Monte Carlo and molecular dynamics calculations using first-principles density functional theory⁴⁶ were also in agreement that hydrogen interactions with the surface do not induce any surface segregation phenomenon (Figure S1c) in contrast to the case of oxygen.³¹ Then, a two-step process is conducted (Figure S2): the HEA NPs were first oxidized in atmospheric air (red box) and then reduced in H_2 environment (gray box). The individual HEA NP at the bottom left and the three HEA NPs at the top are magnified and displayed separately in Figure 2a,b. To confirm oxidation of HEA NPs, energy-filtered transmission electron microscopy (EFTEM) was performed. At $t = 40$ min in the frame in Figure S2, the EFTEM maps shown in Figure S3 include the Fe L-edge, O K-edge, and the overlaid image, suggesting that Fe diffuses out to contribute to the oxide growth. The maps for other metals are not shown due to a decreased signal-to-noise ratio as their L-edge onset is at a higher energy range. Within 10 min of the reduction process in H_2 (first frame in gray box, $t = 80$ min) both oxide layers on the smaller and larger NPs transform from dense to porous structure with cracks at the interface between the oxides and the HEA core. Also, the oxide layer is not fully reduced to metallic phase but only the external surface becomes porous, indicating the reaction front being close to the outer surface. It is also interesting to note that

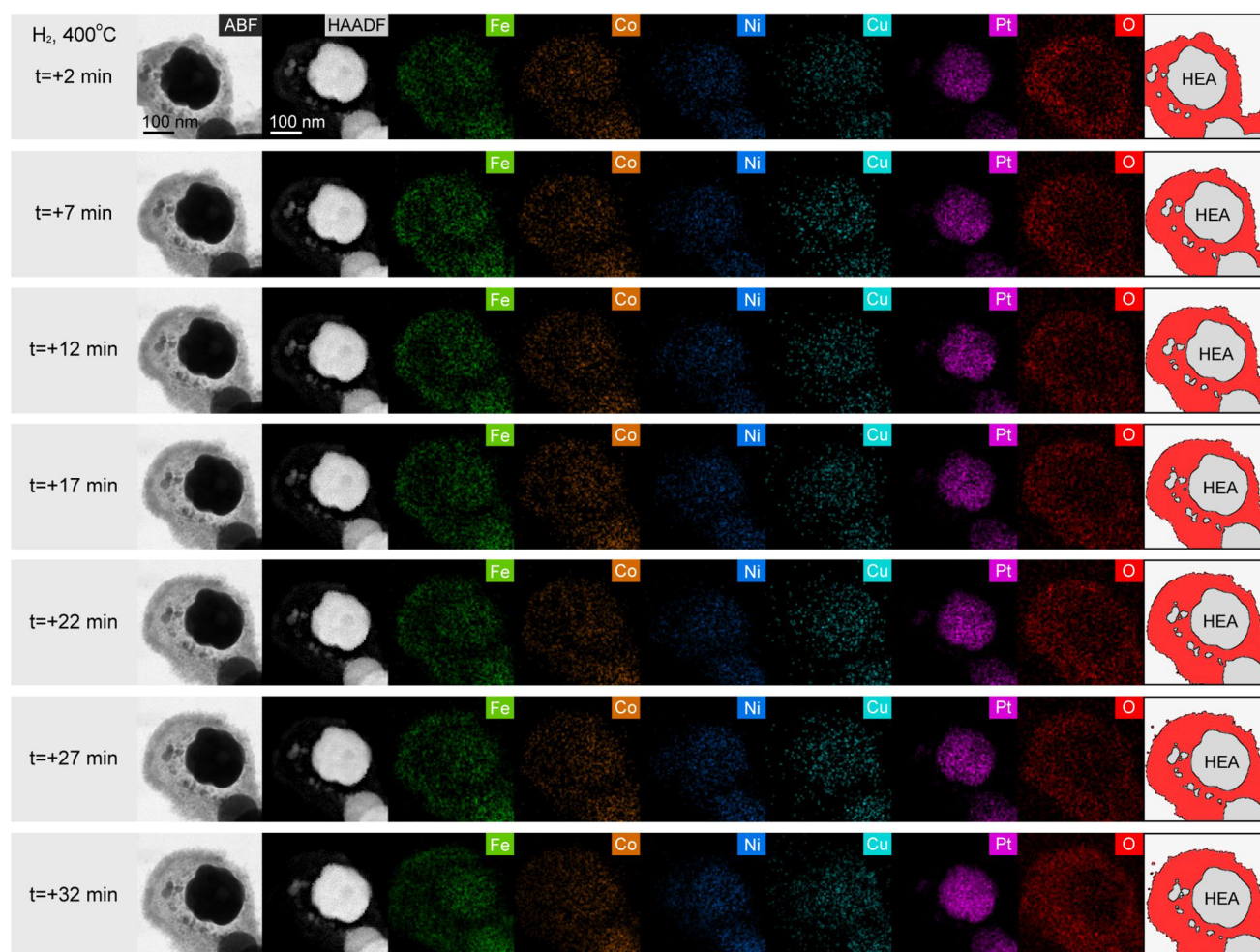


Figure 4. *In situ* EDS maps collected during the reduction HEA NPs in H_2 right after oxidation. First column: time stamp; $t = 0$ is the time when the sample environment changed from air to H_2 . Second column: the ABF and HAADF images of the reduction of HEA NPs in H_2 and EDS maps of each element. Last column: the evolution of HEA NPs and the oxides corresponding to ABF images.

a large number of NP seeds can be seen to form on the oxide external surface as highlighted by the gray arrows. These seeds, ranging from few to tens of nanometers, appear to be unstable as their location changes in time. Figure 2c,d shows the measurement of the oxide thickness (d_{OX}) and NPs diameter (D) evolution during oxidation and reduction. Consistent with our previous work,³¹ the oxidation kinetics follow logarithmic law with a rate constant K close to 2.7 for smaller NP and 13.3 for larger NP. During reduction, the oxide layer on the smaller NP in both directions expands from ~ 10 to ~ 20 nm in thickness after H_2 penetration, accompanied by shrinkage of the HEA core diameter from ~ 178 to ~ 173 nm. Similarly, the oxide layer expands from ~ 50 to ~ 70 nm and further shrinkage of the core of the larger HEA NP can be observed.

To understand the chemical composition of HEA NPs after reduction, the STEM-EDS mappings were performed (Figure 3). The maps in Figure 3a,c were collected at the same region as in Figure 2a,b. It is clear that after H_2 reduction, the HEA NPs segregated into a reduced size HEA core with all five elements and a porous oxide layer containing Fe, Co, Ni. The Cu element, which is shown to be present in the oxide after oxidation,³¹ is not concentrated in the oxide after reduction but instead dispersed widely around the HEA core (Figure 3a), suggesting that the oxidized Cu has been mostly reduced by H_2 . In contrast, Fe, Co, and Ni are not fully reduced and are still preserved in the oxide

region. This is clear in Figure 3c where the NP seed features on the external surface of the oxide mainly consist of Cu element, while Fe, Co, and Ni display a homogeneous mixing within the oxide layer. These results indicate that Cu is the only element that has been fully reduced and segregated into Cu NPs from the oxide. The HEA core, although shrank in size, consists of all five metal elements. The distribution of elements representing the boxed region of the HAADF image is shown in Figure 3b,d. They further indicate that Fe, Co, and Ni are present both in and outside of the oxide, while Cu is only present in HEA core and outside of the oxide layer. This confirms that Cu has been reduced into metallic Cu and segregated outward from the external oxide surface. Atomic distributions from other regions in the HAADF image in Figure 3c show the same trend (details in Figure S4). Furthermore, the HEA core of the HEA NP in Figure 3c displays condensed Pt with atomic ratio more than 23.5% while a significant reduced amount of Fe (12%) and Co (8%) resulted from outward diffusion, which is not obvious on the small NPs shown in Figure 3a with the less significant void collapse (21% Pt, 22% Fe, 18% Co, 18% Ni, 7% Cu). These results suggest that during reduction all transition metals in the oxide react with H_2 and result in the expansion of the oxide layer. Simultaneously, the HEA core contracts and collapses due to the transition metal and associated vacancies' outward diffusion, leaving a gap between HEA core and the oxide internal surface.

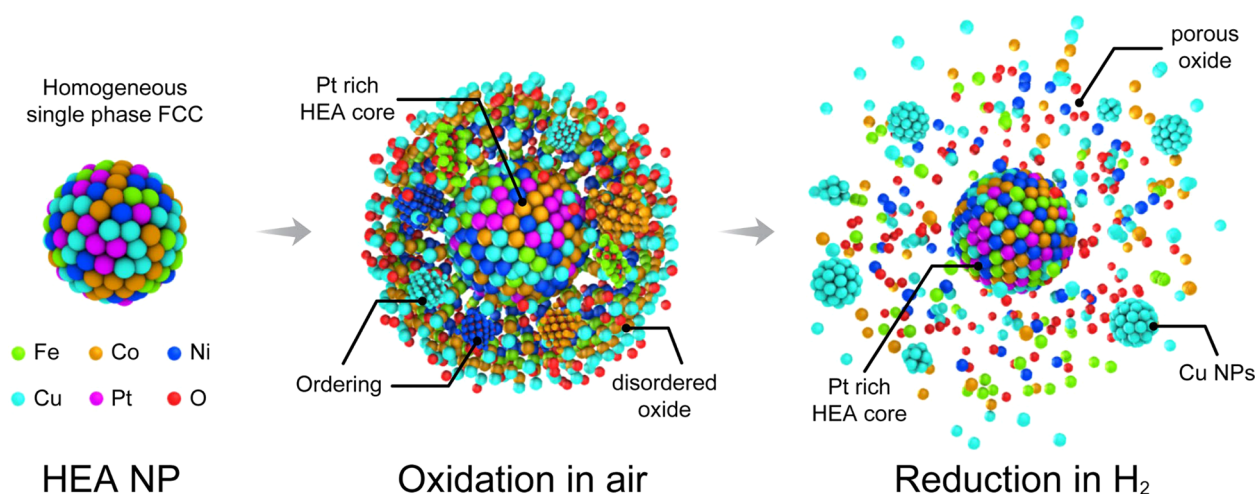


Figure 5. Schematic showing the reduction of oxidized HEA NPs at 400 °C. The oxidized HEA NPs have Pt rich HEA core with disordered oxide layer containing Fe, Co, Ni, Cu. During reduction in H₂, HEA core shrinks due to transition metals' outward diffusion, with expansion of the oxide and segregation of oxidized Cu into reduced Cu NPs.

Next, *in situ* EDS was performed to assist in revealing the compositional evolution. The HEA NPs underwent similar experimental procedures: first they were oxidized in air at 400 °C (Figure S5) and then reduced in H₂ at the same temperature. The oxidation process has been discussed in our previous work where transition metal diffusions are fully confirmed,³¹ and here the reduction process is shown in Movie S1. Figure 4 shows the EDS maps taken from HEA NPs. When the oxidized HEA NPs are exposed to H₂, it is obvious that the oxide expands as transition metals are reduced. Additionally, a concentration gradient between the HEA core and oxide layer drives further outward diffusion, resulting in depletion of transition metals at the internal oxide surface but enrichment at the external oxide surface. Therefore, a deficiency of elements between the HEA core and the internal oxide surface is observed, resulting in further segregated HEA core and oxide shell configurations.

Combining the information from real-time imaging and analytical EDS, the behavior of oxidized FeCoNiCuPt HEA NPs in H₂ can be illustrated in Figure 5. During reduction, all transition metals in the oxide react with H₂ and Cu can be fully reduced and further segregated into Cu NPs. Most Fe, Co, and Ni are still preserved in the oxide form. On the basis of the Ellingham diagrams,⁴⁷ Cu oxide is the least stable among other metal oxides at 400 °C and thus preferable to reduce. Because of the disordered character of the oxide confirmed in our previous work,³¹ H₂ penetration into and water diffusion out of the oxide are difficult,⁴⁸ resulting in the reaction front being at the external surface of oxide and formation of porous structures only at regions close to the outer surface. In addition, due to different diffusivity of cation and anion during oxidation vacancy injection is a common process³⁵ that can lead to a porous structure of the oxide. However, upon reduction this process is not reversed and can be another explanation of why the boundary for reduction is maintained at the oxide shell. The expansion of the oxide layer and simultaneous shrinkage of the HEA core are expected to be due to a change of concentration gradient that drives further transition metals' diffusion, and condensation of vacancies resulting in a gap between the HEA core and the oxide internal surface. As a result, the final products are HEA cores surrounded by porous oxides containing oxidized Fe, Co, and Ni with further segregated metallic Cu NPs at the external oxide surface. Besides EDS, we believe future investigations utilizing STEM-EELS to

analyze the energy-loss near-edge fine structures of the metal elements³¹ will provide more insight of the oxidation states after reduction.

CONCLUSION

The present work provides *in situ* TEM investigation of oxidized HEA NPs during reduction in atmospheric H₂ at constant temperature of 400 °C. The oxide layer transformation into porous structures is observed as H₂ penetrates into the oxide layer but the reaction front mostly remains at the external surface of the oxide. Oxidized Cu can be fully reduced and further segregated into Cu NPs, while Fe, Co, and Ni remain in the oxide phase. Further expansion of the oxide layer and size reduction of HEA core during H₂ reduction were observed resulting in segregated HEA core and oxide shell. The present study facilitates an in-depth understanding of HEA reduction mechanisms under reducing environment, and can provide insights into designing high corrosion resistance alloys, H₂-resilient structural materials, hydrogen storage materials, and durable catalysis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.nanolett.0c04572>.

In situ EDS maps of HEA NPs during reduction in H₂ at 400 °C (MP4)

Materials and Methods; *in situ* TEM image series of HEA NP reduction in H₂ at 400 °C. (Figure S1); *in situ* TEM image series of HEA NPs oxidation in air and reduction in H₂ (Figure S2); TEM image and EFTEM maps of HEA NPs collected during oxidation (Figure S3); EDS linescan showing Fe, Co, Ni, Cu, Pt, and O atom % (Figure S4); *in situ* EDS maps of HEA NPs oxidation in air (Figure S5) (PDF)

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Author Contributions

B.S. and R.S.-Y. developed the idea for this project. Y.Y. and M.Z. synthesized the specimens. B.S. performed all the electron microscopy studies. T.Y. and W.S. performed the DFT studies. Y.L., K.H., X.H., Y.Y., and V.D. assisted the electron microscopy efforts. B.S. completed the writing of the manuscript under the supervision of R.S.-Y. All of the authors made contributions to the discussion and interpretation of results and modified parts of this paper.

Notes

The authors declare no competing financial interest.

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