



Enhanced photocatalytic abilities of innovative NbTaZrMoW high-entropy alloys (HEAs): a comparative analysis with its high entropy oxide (HEO) counterpart

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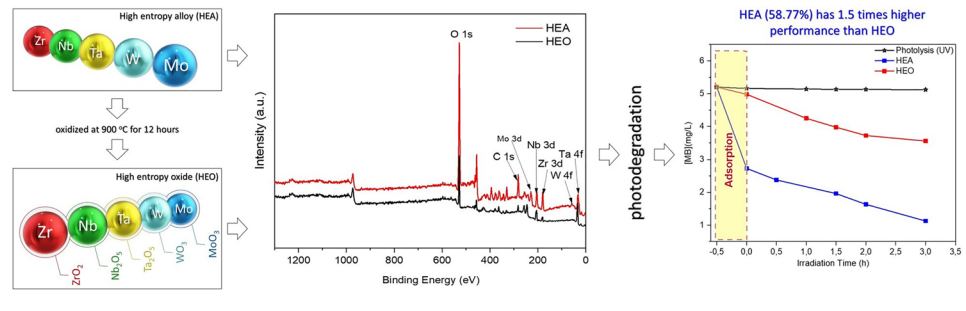
ABSTRACT

The photocatalytic performance of high entropy alloy (HEA) and its oxide form (high entropy oxide, HEO) have been evaluated in this study. The HEA, composed of Nb, Ta, Zr, Mo, and W powders, was synthesized through a mechanical alloying process for 120 h. This process was carried out under a high-purity Ar atmosphere to prevent oxidation. Subsequently, the HEA was converted into HEO via a mechano-thermal oxidation method 900 °C for 12 h. The photocatalytic activity of both oxidized and non-oxidized samples was systematically evaluated by degradation of methyl blue (MB) under UV irradiation. Electron dispersive spectroscopy (EDS), X-ray diffraction (XRD), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS) were used to investigate the structural and chemical features of the alloys. Furthermore, BET surface area analysis and Zeta potential measurements were conducted to understand the alloys' surface properties and stability in aqueous solutions. The results showed that the HEA has a remarkable photodegradation performance of around 58.77% which is two times higher than that observed with the HEO.

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GRAPHICAL ABSTRACT



Introduction

Conventional alloys are designed by mixing a base metal with at least one additional metal to enhance its mechanical or other desirable properties. The alloying level of the metals is limited by their solubility limits. Additionally, precipitate or intermetallic phases and complex microstructures can be formed, which adversely affect various properties such as mechanical strength and corrosion resistance [1–3]. But what do we get if we step outside of traditional compositions and design alloys from multiple elements rather than just one or two ‘basic’ elements? The answer to this question was found with this new concept, first proposed in 1995, called high entropy alloy (HEA) [4–6].

HEAs are defined as alloys formed by at least five different equimolar or near-equimolar elements. Each element forming the alloy can be present in the alloy with atomic 5–35%. The mixing entropies of HEAs in liquid or random solid solution phases are substantially larger than those in traditional alloys. For this reason, HEAs have much higher strength than classical alloys [7, 8], so good wear resistance [9, 10], perfect structural stability [11], wonderful corrosion resistance, and antioxidation [12–14], and they exhibit characteristics.

The HEAs can be divided into two different groups. These are: (1) traditional HEAs consisting of 3d-transition metals, and (2) refractory HEAs (RHEA) consisting of refractory metals. Although the properties of the first group HEAs are superior to conventional alloys, they are poor compared to RHEAs. However, they are cheaper than RHEAs. RHEAs have high potential for many high-temperature applications, nuclear applications, and aerospace applications [15].

Another significant class of high-entropy materials is high-entropy ceramics (HECs). These ceramics

contain five or more cations and exhibit superior properties compared to traditional ceramics [16]. Among the various types of high-entropy ceramics, high-entropy oxides (HEOs), nitrides (HENs), carbides (HECs), borides (HEBs), hydrides (HEHs), silicides (HEsIs), sulfides (HEsS), and hydrides (HEHs) are notable [16, 17]. They find applications as coatings or high-temperature materials due to their higher hardness, elevated melting points, and superior resistance to oxidation and corrosion [16].

Currently, high-entropy oxides (HEOs) represent one of the most researched categories of HECs, offering promising potential across diverse such as hydrogen production [18], magnetic or dielectric components [19, 20], batteries [21], or thermal barrier coatings [22]. However, there haven’t been any serious attempts to determine the photocatalytic capabilities of HEOs and compare them with their non-oxidized counterparts (HEA). Exploration in this area could lead to the development of novel and efficient photocatalysts with wide-ranging practical applications and improve their performance.

Edalati et al. [23] synthesized TiZrNbHfTaO₁₁-based HEOs using a high-pressure and oxidation process and explored their efficacy in photocatalytic CO₂ conversion. The results indicated that the activity of HEO is better than BiVO₄ and anatase TiO₂ photocatalysts due to its defective and strained dual-phase structure, and appropriate electronic band structure. Similar results have been reported for TiZrNbHfTaO₆N₃-based oxy-nitride compounds [24, 25]. The obtained data revealed that HEAs derived from refractory metals exhibit remarkably high photocatalytic performance in comparison with conventional photocatalysts such as benchmark photocatalyst P25 TiO₂ or reported photocatalysts in the literature. In their study, Edalati and colleagues [23, 25] employed a high-pressure torsion

(HPT) process on a blend of elemental metal powders constituting the HEA alloy. Subsequently, the resulting HEA pellet was oxidized in air at 1100 °C for 24 h, leading to the oxidation of only the surfaces of the powder particles. This selective oxidation occurs due to the refractory nature and high-temperature resistance of the metals comprising the alloy. During the initial stages of oxidation, it is plausible that a refractory oxide layer forms around the surface of the powders, hindering the penetration of oxygen toward the inner regions of the particle. These studies indicated the importance of understanding the intricate between material composition, fabrication techniques, and photocatalytic performance. Therefore, it is crucial to understand the photocatalytic effect of the obtained HEO when the oxidation process predominantly influences the entire structure. Thus, further investigations into the mechanisms underlying the enhanced photocatalytic properties of HEOs, particularly concerning their structural and electronic characteristics, are essential for harnessing their full potential in various practical applications.

Therefore, in the present study, HEAs were prepared through mechanical alloying, unlike the HPT method and a mechano-thermal approach was employed to allow the entire structure to be oxidized. This was assumed to reveal the complete photocatalytic effect of the oxide structure. The results are discussed in detail below.

Experimental procedure

Production of high entropy alloys (HEAs) and high entropy oxides (HEOs)

Step-1: HEA production: Zr (99.5% purity, Nanografi comp.), Nb (99.5% purity, Nanografi comp.), Ta (99.5% purity, Nanografi comp.), Mo (99% purity, Merck), W (99% purity, Merck) elemental powders are commercially available. Powders weighed equimolarly were placed in the vial. The mechanical Alloying (MA) process was carried out in a Retsch PM 100 brand high-energy mill for 120 h. The MA process was performed at 300 rpm with a ball/powder ratio of 20/1, 12 mm steel balls were used. To prevent oxidation, the MA process was carried out under an Ar atmosphere. 2% by weight zinc stearate was added as a grinding agent. At the end of the 120-h MA process, HEA with ZrNbTaMoW composition was produced.

Step-2: HEO production: HEAs produced in Step-1 were converted into HEO by mechano-thermal process. The produced HEAs were oxidized at 900 °C for 12 h. At the end of the process, it was taken from the oven and ground in an air atmosphere in a high-energy mill at 300 rpm for 3 h. After the milling process, they were oxidized again at 900 °C for 12 h.

Photocatalysis study

The photocatalytic performance of oxidized and non-oxidized ZrNbTaMoW HEA was assessed under UV irradiation by degradation of the MB dye in aqueous solution. A 5 mg·L⁻¹ was the starting MB concentration. To form an adsorption–desorption equilibrium between the photocatalyst and MB, the photocatalyst was added to the reactor holding 100 ml of MB and magnetically agitated for 30 min in the dark prior to irradiation. The solution was then exposed to UV light generated by a 300 W Ultra-Vitalux lamp equipped with a high-pressure tungsten filament source for 3 h. The reactor temperature was maintained at 25 °C by constant water flow. At each 30-min interval, 4 ml solution samples were taken for subsequent analysis, and a UV–visible spectrophotometer was used to measure MB absorbance at 664 nm.

Mott-schottky analysis of HEA and HEO

The Mott-Schottky analysis of the HEA and HEO was carried out in a 0.1M Na₂SO₄ at 1 kHz in the potential range.

of −1.0 to +1.0 V versus SCE. A conventional three-electrode cell consisting of a saturated calomel electrode (SCE) as the reference electrode, a platinum sheet (4 cm²) as the counter electrode, and a glassy carbon electrode (0.07 cm²) was used for the electrochemical analysis. All the electrochemical experiences were performed at least three times at room temperature (298 K). For the fabrication, the glassy carbon electrode was first well-polished using 1 μm alumina powder then a polishing cloth to obtain a mirror-like surface. The working electrode was next ultrasonicated in deionized water and ethanol for 15 min, successively, and then dried at room temperature. Then, HEA or HEO was dispersed in ethanol to obtain a concentration of 1 mg·mL⁻¹, which was sonicated for 15 min to obtain a homogeneous solution. Finally, 10 μL of the dispersed HEA or HEO were drop-casted on the

cleaned glassy carbon electrode using a micropipette and dried at 50°C for 5 h.

Characterization

At the beginning and the end of the mechanical alloying process, the powders were subjected to X-ray spectra (XRD, Rigaku Miniflex 600), Scanning Electron microscope (SEM, Hitachi SU3500), Electron dispersive spectroscopy (EDS, Oxford AZtech) examinations. The obtained oxide powders were subjected to XRD and SEM analyses. Additionally, they were subjected to X-ray photoelectron spectroscopy (XPS, Specs-Flex) analysis to characterize the oxides formed. The surface area and porosity of the examined samples were determined using the Brunauer–Emmett–Teller (BET) method. This analysis was made with the micromeritics 3Flex brand BET device using N₂ adsorption and desorption isotherms. Additionally, the derived pore volumes were calculated using the Barrett-Joyner-Halenda (BJH) method. The particle size distribution (d) and zeta potential (ξ) of the investigated HEA samples were conducted at ambient temperature and repeated three times. Zeta potentials were measured with a Malvern Nano ZS to find the isoelectric point of the adsorbent.

Results and discussion

Figures 1 and 2 illustrate the X-ray Diffraction (XRD) spectra for both the initial raw materials (ZrNbTaMoW) and the HEA synthesized through the

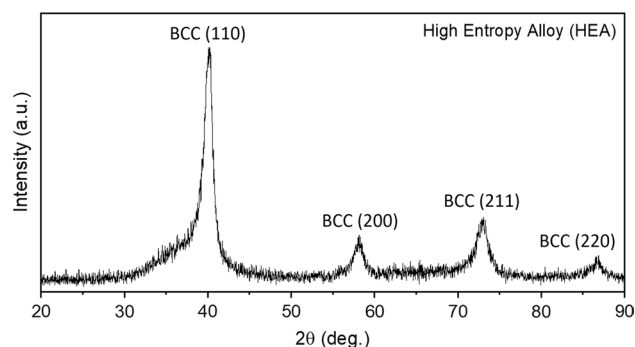


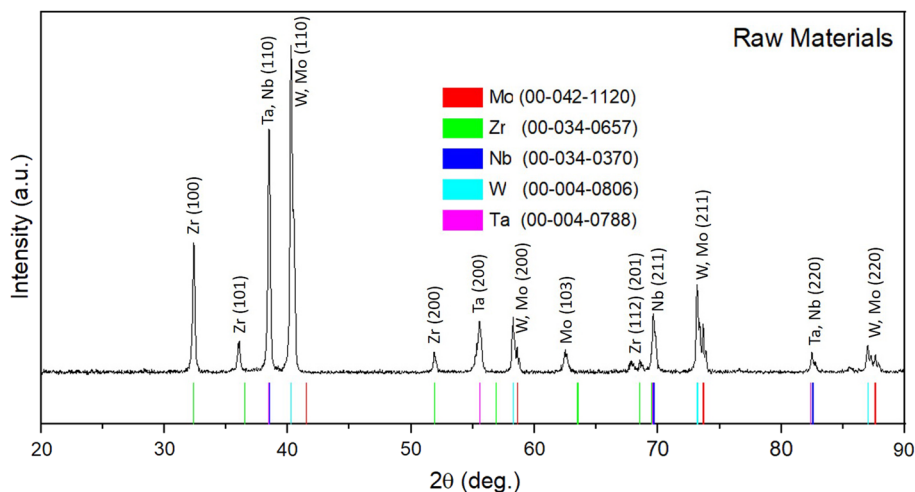
Figure 2 XRD spectra of synthesized HEA from Zr, Nb, Ta, Mo, W raw materials.

mechanical alloying process for 120 h using the raw material composition, respectively.

The XRD spectrum reveals the presence of distinct peaks associated with individual elemental powders at the outset of the mechanical alloying (MA) process. After subjecting the materials to 120 h of MA treatment, the structural composition became dominated by three prominent peaks. These peaks are as follows: a broad and relatively intense (110) peak situated around 42°, the (200) peak at approximately 58°, and the (211) peak at roughly 73°. Notably, these three peaks correspond to the body-centered cubic (BCC) crystal structure commonly observed in high entropy alloys [26, 27]. Since the elements forming the alloy have a refractory character, it is an expected result that the resulting alloy will have a BCC structure.

Figure 3 shows the SEM image of the HEA synthesized through the 120 h mechanical alloying process. The image reveals particle agglomeration with

Figure 1 XRD spectra of initial raw materials.



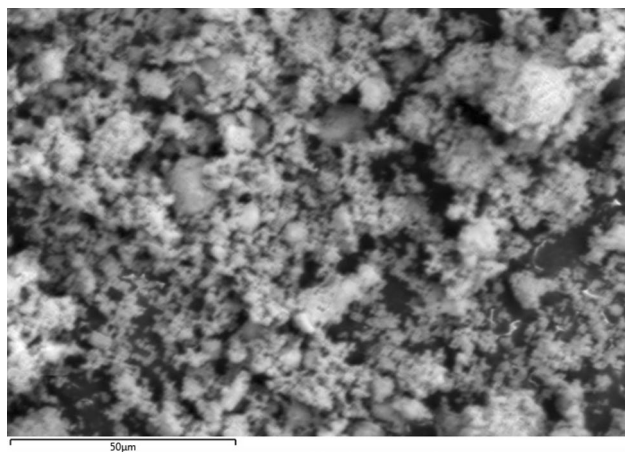


Figure 3 SEM image with EDS spectrum of the HEA after 120 h of mechanical alloying.

diameters ranging between 10 and 15 μm. Furthermore, the elemental mapping results, as depicted in Fig. 4, indicated a uniform distribution of all metals within the alloy. This uniform distribution is particularly noteworthy as it signifies the effectiveness of the extended MA process (120 h) in achieving a well-mixed and integrated composition. By the way, it is important to note that all processes were carried out under controlled atmosphere conditions in this study. However, despite taking all possible precautions to minimize carbon contamination, very small traces of carbon contamination were detected in the mapping analysis, likely attributable to organic residues or external factors during sample preparation or handling.

The oxidation of HEA at 900 °C for 12 h resulted in the formation of high entropy oxide (HEO), denoted

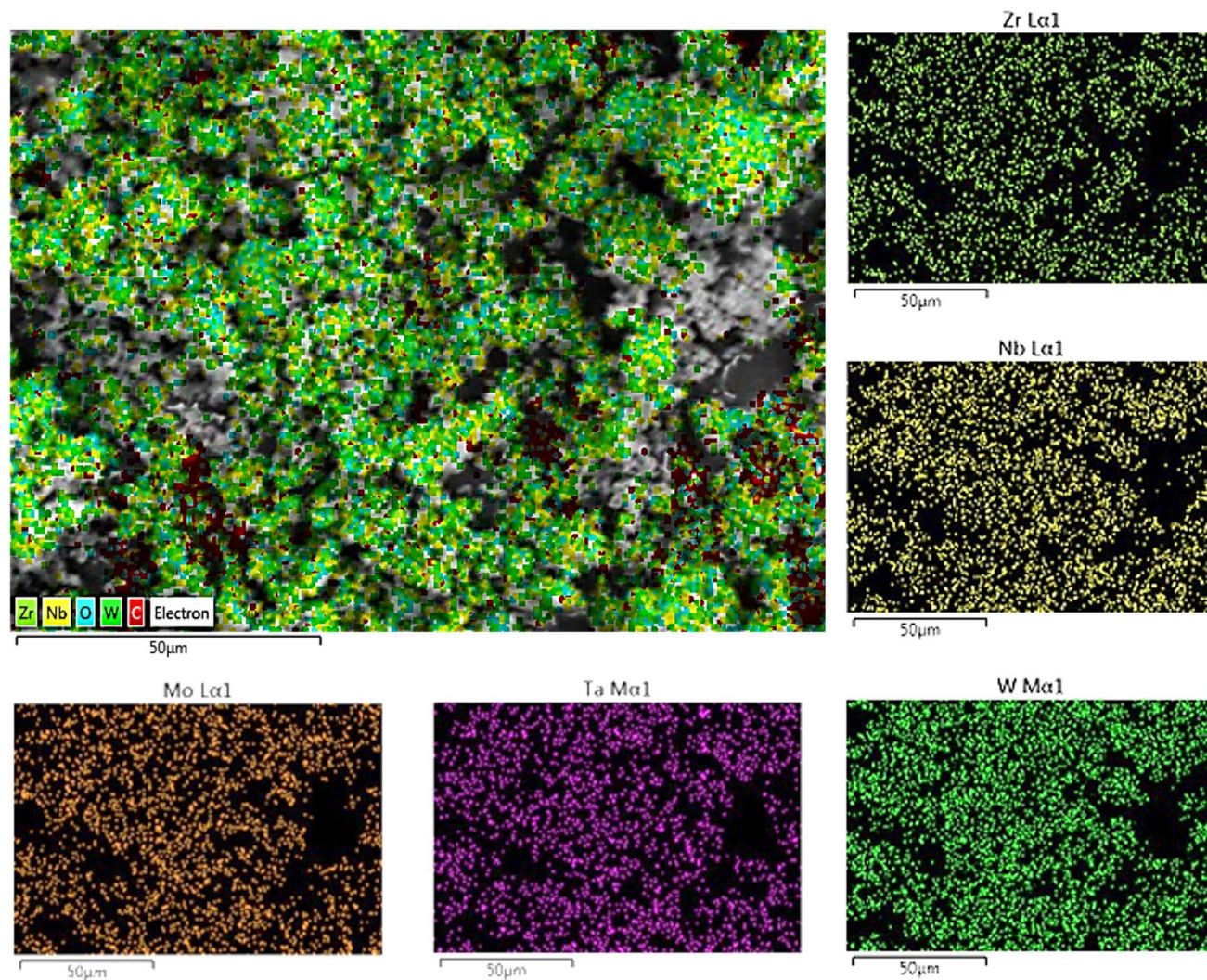


Figure 4 Elemental mappings from SEM image in Fig. 3.

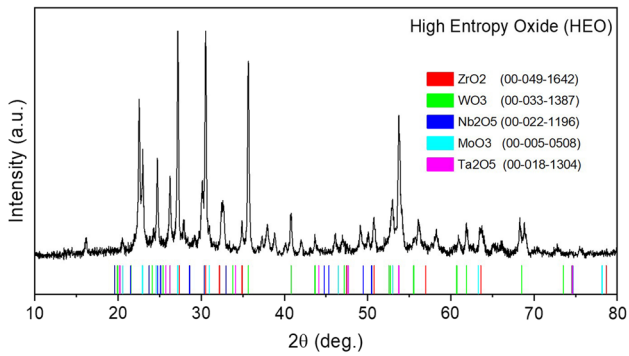


Figure 5 XRD spectra of synthesized HEO from HEA materials.

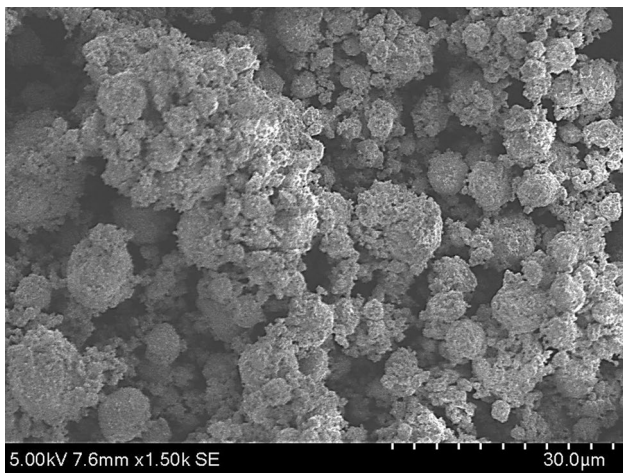


Figure 6 SEM image of the HEO after 12 h of oxidizing at 900 °C.

as ZrNbTaMoWO_x oxide. The XRD spectrum of the obtained HEO is presented in Fig. 5. In contrast to the XRD pattern of the HEA (Fig. 2), the HEO exhibited multiple distinct crystalline peaks, indicating its diverse oxide composition. Analysis revealed that these peaks corresponded to several oxides, primarily ZrO₂, WO₃, Nb₂O₅, MoO₃, and Ta₂O₅, as depicted in Fig. 5.

Figure 6 presents the SEM image of the HEO, revealing particles of a few micrometers in size with agglomeration. While the particles exhibit a nearly spherical shape, their cluster were not uniform dispersion.

Furthermore, the elemental mapping results in Fig. 7 suggest a uniform distribution of all metals within the alloy. Moreover, while oxygen appears to be predominant in the alloy, area EDS analyses were conducted to validate this observation, and compared with its unoxidized form (Fig. 8).

The EDS analysis revealed an oxygen atomic ratio of approximately 15% (by weight, ~ 5%) for HEA, while in the case of HEO, this ratio was significantly higher, approximately 84% (by weight, ~ 45%). Although the HEA synthesis is conducted under a protective atmosphere, due to the extended milling duration (120 h), some oxygen ingress into the system becomes inevitable. Since the raw materials used for producing the alloy were in powder form. It is well-known that oxides are present on the surfaces of metal powders even without processing. Furthermore, the metal powders underwent a mechanical alloying process, significantly increasing the surface area and introducing defects into the structure, which further enhances the powders' affinity for oxygen during the process. Additionally, the oxygen content could potentially be attributed to several

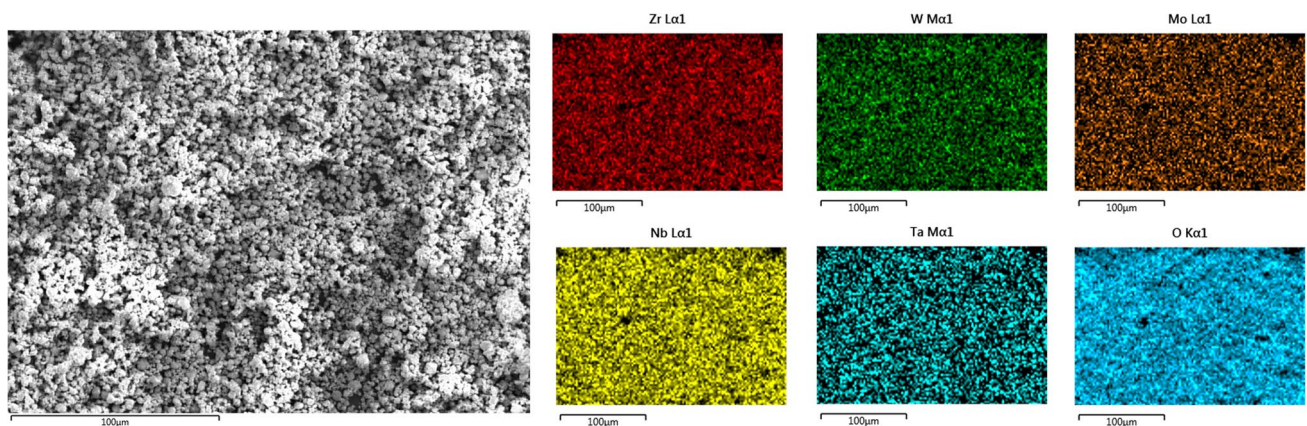


Figure 7 Elemental mappings of HEO.

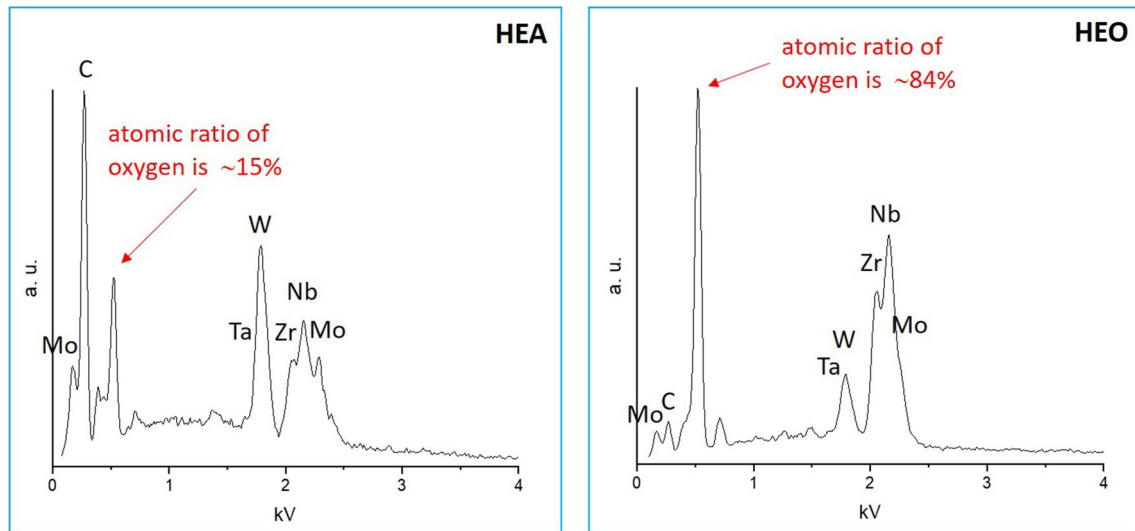


Figure 8 Comparison of oxygen ratios in HEA and HEO based on EDS analyses of SEM images (presented in Figs. 3 and 6).

factors, including surface contamination, oxygen adsorption during sample preparation, or the presence of oxygen in interstitial sites within the alloy lattice, unavoidably. Even so, the big differences in the oxygen content can be seen clearly in Fig. 8 and confirm the mechano-thermal process.

According to SEM–EDS analysis, the produced materials generally consisted of HEA and HEO initial constituents. It is well known that one general prerequisite of high-entropy materials is the uniform distribution of components. The distributions were confirmed by mapping results. Even so, the challenges associated with the identification of oxide structures using EDS led to employing XPS analysis for the comprehensive characterization of the HEO structure. It is well known that XPS analysis offers a susceptible and surface-specific technique for determining materials' elemental composition, chemical states, and bonding environments. Figure 9 illustrates the full XPS spectrum of the HEO and HEA materials, which shows the existence of Zr, Nb, Ta, Mo, W, and C peaks. C 1s peak can be attributed to the inevitable carbon contamination on the alloy surface. Besides, the narrow scanning spectra of alloy elements both HEA and HEO were compared in Fig. 10.

The high-resolution XPS spectrum of Nb 3d in non-oxidized HEA can be deconvoluted into three peaks at 201.95, 205.53, and 208.42 eV which are assigned to Nb⁰, Nb⁺⁴, and Nb⁺⁵, respectively

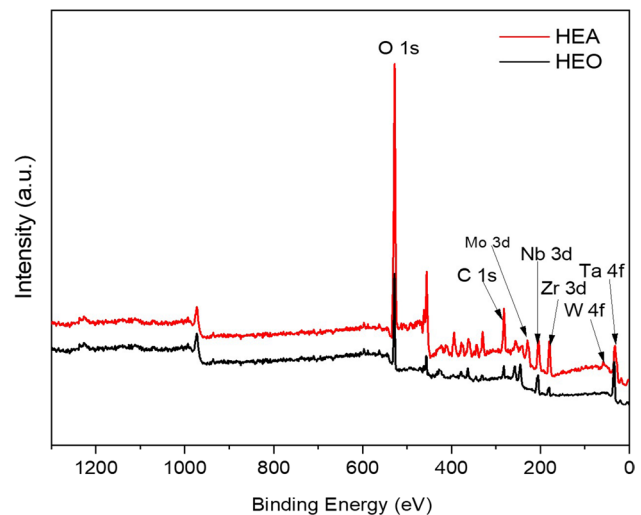


Figure 9 XPS full spectrum of the surface of the HEA and HEO.

(Fig. 10a) [23, 28]. However, the spectrum of Nb 3d in oxidized HEA shows the presence of peaks characteristics of Nb⁺² and Nb⁺⁵ (Fig. 10b). The Zr 3d spectrum (Fig. 10c, d) had the strong spin-orbit doublet Zr 3d_{3/2}–Zr 3d_{5/2} with the splitting of about 2.56 eV characteristic to Zr⁺⁴ [29, 30]. In Fig. 10e, the peaks at 230.4 eV and 241.6 eV binding energies correspond to the presence of Ta (4d_{5/2} and 4d_{3/2}, respectively). However, the red and brown regions plotted indicate the existence of the Ta-metal layer. EDS analyses revealed minimal oxygen ingress into

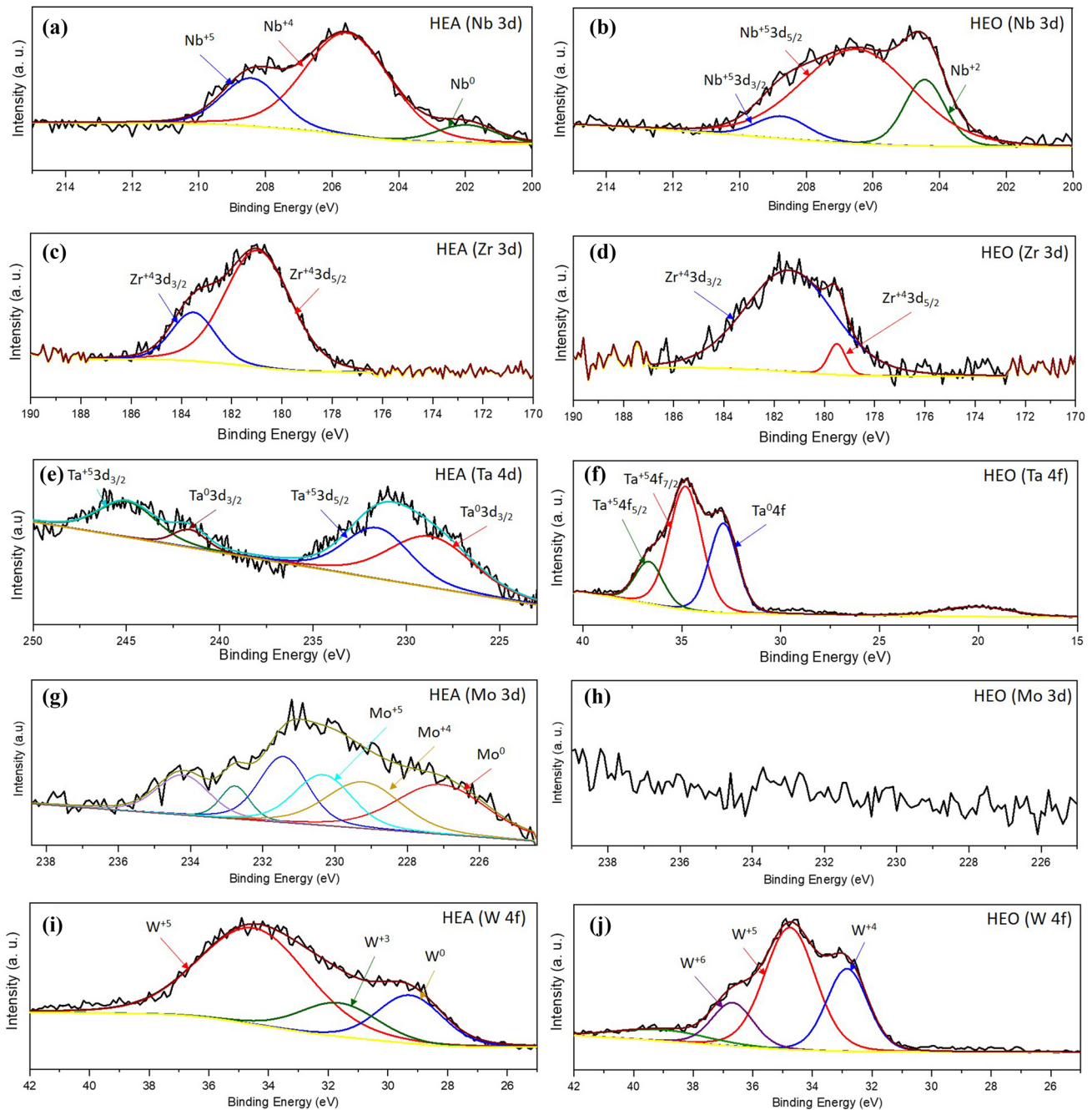


Figure 10 The narrow scanning spectra of the HEA and HEO samples, respectively: **a** and **b** Nb 3d, **c** and **d** Zr 3d, **e** and **f** Ta 4f, **g** and **h** Mo 3d, **i** and **j** W 4f.

the HEA system, as shown in Fig. 8. Because it could not observe the 4d 5/2 peak of Ta in HEO (Fig. 10f). Additionally, Fig. 10 g revealed the Mo 3d peaks representing the metal, Mo^{+4} , and Mo^{+6} states of the HEA [31, 32]. Notably, the XPS peaks corresponding to the oxide structures of Ta and Mo were not

observed in the HEO configuration (Fig. 10f and h). Instead, vibrations were predominantly observed. This phenomenon can be attributed to two possible reasons. Firstly, it is likely due to extensive oxidation, leading to the formation of thick and stable oxide films on the surfaces of Mo and Ta, rendering

these elements undetectable. Secondly, the close proximity of the binding energy levels of Ta, Nb, and Mo elements in the HEA system occasionally results in overlapping signals. The W spectra in HEA can be segmented into three distinct peaks representing W^{+5} (34.50 eV), W^{+3} (31.64 eV), and metallic W (29.26 eV) (Fig. 10 i) [33]. On the other hand, the deconvoluted

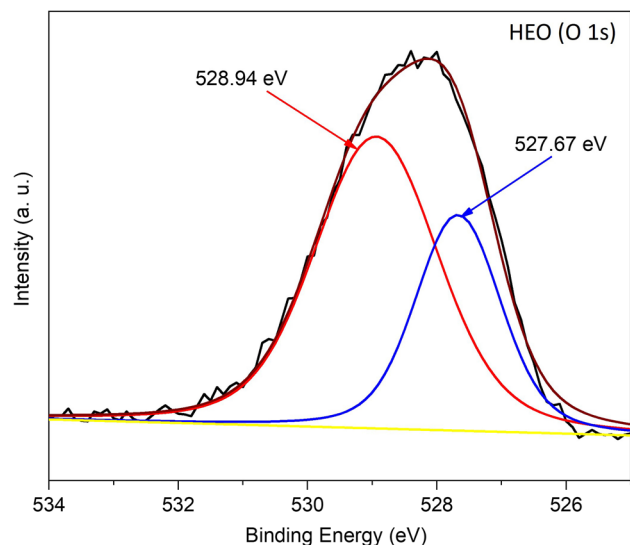


Figure 11 The narrow scanning spectra of O 1 s for HEO sample.

spectrum of W in the oxidized HEA shows the presence of W^{+4} , W^{+5} , and W^{+6} (Fig. 10j) [34]. The high oxidation state of all elements observed in the oxidized samples might be attributed to the process of thermal oxidation.

For the oxidized sample, the peak position of the O1 peak was successfully deconvoluted into two peaks (Fig. 11). The first peak localized at around 527.67 eV belongs to the O^{2-} while the peak at 529 eV can be attributed to the adsorbed hydroxylated groups [35–37].

The surface area and porosity of the examined samples were determined using the Brunauer–Emmett–Teller (BET) method. In Fig. 12, nitrogen sorption isotherms conducted at 76 K demonstrate a type III isotherm pattern for both HEA materials. The repeated lines in Fig. 12a correspond to the adsorption and desorption cycles, with forward sweeps indicating adsorption and backward sweeps indicating desorption. Thus, the observed sharp rise at small pore diameter in Fig. 12b for HEO could potentially be attributed to specific characteristics of the material, such as its pore size distribution or surface properties, which influence the adsorption–desorption behavior elucidated by the BET analysis. The figure indicated that HEA exhibited a BET surface area of $3.628 \text{ m}^2 \cdot \text{g}^{-1}$, which decreased by $1.033 \text{ m}^2 \cdot \text{g}^{-1}$ following the incorporation of the oxygen element (HEO).

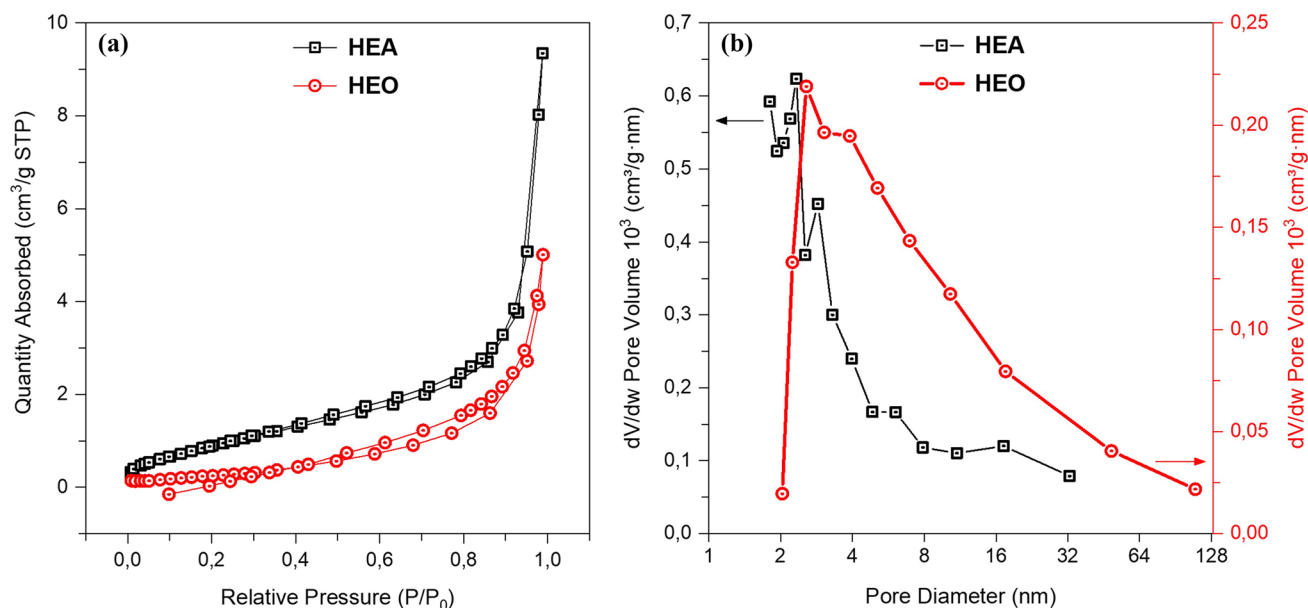


Figure 12 **a** The Brunauer–Emmett–Teller (BET) surface area measured from nitrogen adsorption–desorption isotherms and the **b** the corresponding pore size distribution of HEA and HEO samples.

Additionally, the derived pore volumes, calculated using the Barrett-Joyner-Halenda (BJH) method, were determined to be $0.0142 \text{ cm}^3 \cdot \text{g}^{-1}$ for HEA and $0.0077 \text{ cm}^3 \cdot \text{g}^{-1}$ for the HEO.

The particle size distribution (d) and zeta potential (ξ) of the investigated HEA samples were conducted at ambient temperature and repeated three times,

as illustrated in Fig. 13a, b. The summarized values obtained from each analysis are presented in Table 1. It is noted that the three records in the figure represent three measurements aimed at determining the median value. Additionally, the differences observed in the intensity profiles of HEA could potentially stem from factors such as the presence of agglomeration,

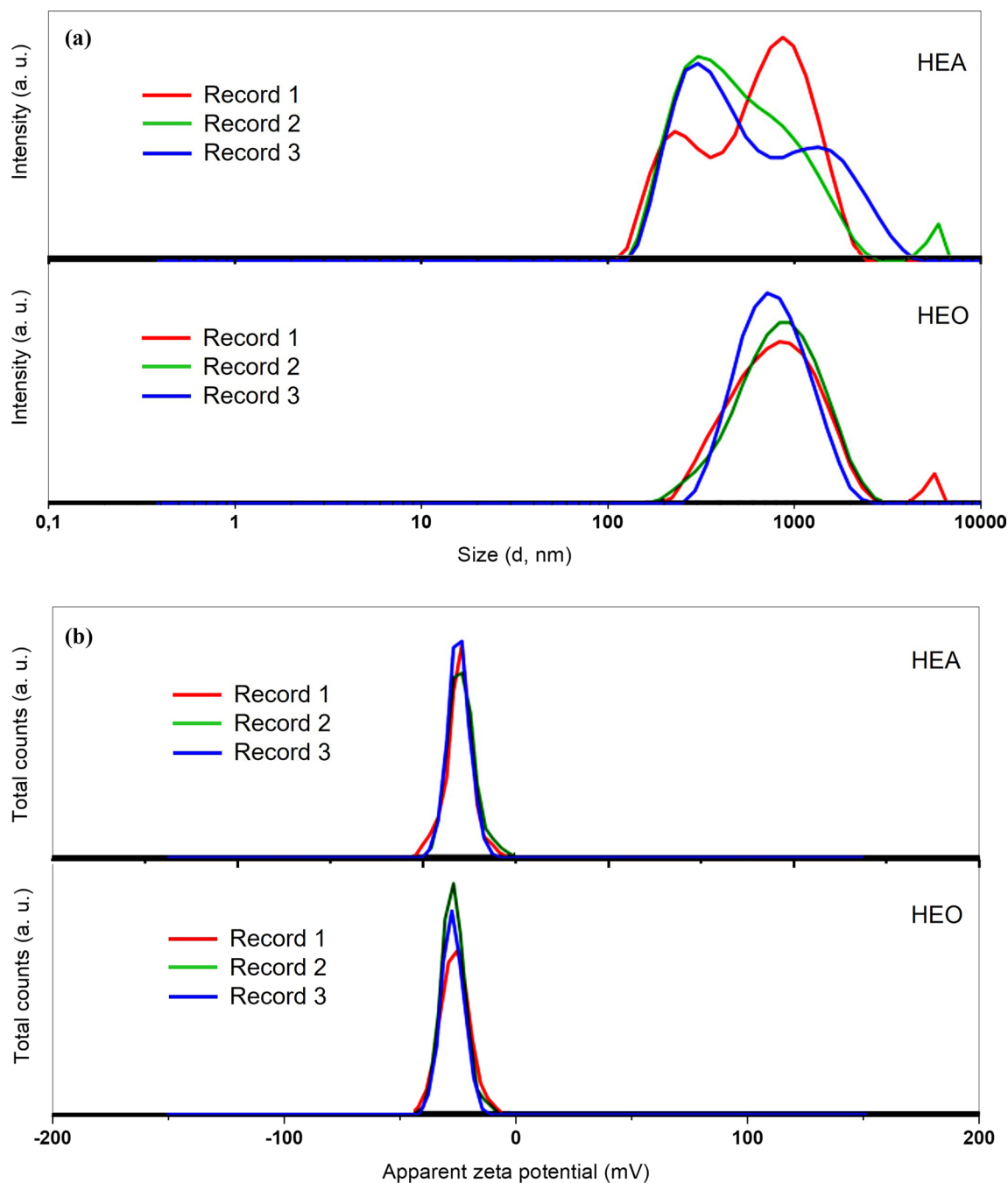


Figure 13 **a** The particle size distribution and **b** apparent zeta potential (ξ) of HEA and HEO samples.

Table 1 The particle size distribution (*d*) and zeta potential (ξ) obtained for oxidized and non-oxidized ZrNbTaMoW HEA

Record	HEA			HEO		
	1	2	3	1	2	3
<i>d</i> (nm)	472.5	437.4	445	797.1	738.9	716.6
ξ (mV)	−25.1	−24	−25.3	−26.2	−26.9	−27.3

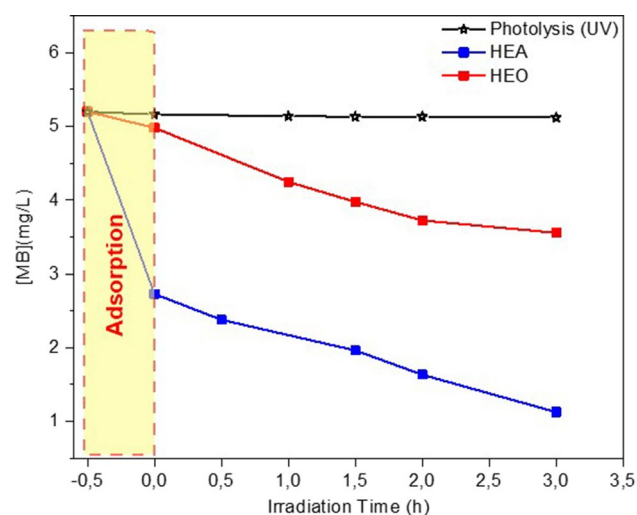


Figure 14 Degradation of MB by photocatalysis on the HEA and HEO surfaces, [MB] = 5 mg·L^{−1}, Xe lamp 300 W.

as previously observed in SEM analysis (Fig. 6). This might have contributed to non-uniform data records in certain analyzed spots.

HEA demonstrated an average size distribution of 451.6 nm, whereas the HEO exhibited an enlarged size distribution, with an average value of 750.9 nm. This increase in size distribution could potentially be attributed to the incorporation of oxygen atoms, leading to an expansion in the grain size. Furthermore, the presence of a significant amount of oxygen content also influenced the zeta potential of the studied HEA. This resulted in a slight increase in the average zeta potential value, shifting from −24.8 mV in the HEA to −26.8 mV in the HEO sample. This change can be rationalized by considering the electronegative nature of the oxygen element.

The photocatalytic activity of both oxidized and HEA materials was evaluated in the photodegradation of MB under UV irradiation. As shown in Fig. 14, the concentration of MB changes over irradiation time in the presence and absence of the photocatalysts.

The initial photolysis process led to approximately 2% degradation of MB. However, the introduction of

catalysts noticeably enhanced the degradation of MB. The degradation curves demonstrated that the photodegradation rate of MB was slower after 1.5 h UV light exposure (Fig. 14). The decrease rate could be due either to the MB competing with other photoproducts for the available photons or to binding between MB molecules and surface of catalyst [38]. Interestingly, with the presence of the catalysts, the results indicated that the HEA sample exhibited significantly higher adsorption and photocatalytic activity compared to the oxidized counterpart (HEO). After 3 h, the HEA displayed a remarkable photodegradation performance of around 58.77%, which is approximately two times higher than that observed with the HEO. This superior efficiency of the HEA can be attributed to its larger surface area when compared to the HEO, as indicated by the BET analysis. Another factor responsible for the decrease in photocatalytic activity is the reduction in sample heterogeneity after annealing, which leads to a decrease in the number of nanoscale galvanic cells, as reported by Wang et al. [37].

By the way, generally, oxide structures are expected to exhibit higher photocatalytic performance compared to non-oxide metal alloys [16]. This is attributed to the presence of active sites within oxide structures, enhanced by crystal defects and lattice strains, which are typically lacking in non-oxide metal alloys [39, 40]. However, in Fig. 14 is considered, the findings of this study may appear contrary to this phenomenon. Since HEA exhibited significantly higher photocatalytic activity compared to HEO in the present study. To explain this performance of HEA, various factors were taken into consideration. In other words, the photocatalytic performance of two materials with different compositions, HEA (ZrNbTaMoW) and HEO (ZrNbTaMoWOx), were compared in this study. The HEAs were produced through prolonged mechanical alloying (120 h), resulting in the material containing high levels of strain and defects. The increased lattice strains and defect density in HEA might have enhanced the photocatalytic activity. Since the formation of inherent point defects act as active sites for

catalysis [41]. However, HEO was obtained through the oxidation of HEA at 900 °C. During the oxidation process, while the surface of HEA particles oxidized, the interior regions re-crystallized due to the temperature effect, potentially leading to reduced defects and lattice strains. The XRD spectra presented in Figs. 2 and 5 confirm these differences. HEA's XRD spectrum consists of broad and low-intensity peaks, indicating the presence of amorphous structures, whereas HEO's XRD spectrum displays sharp, narrow, and intense peaks, indicative of crystalline structures. Similarly, Wang et al. [37] reported that the synergy of solid solution and formed amorphous phases during the ball-milling promotes the photocatalysis response of HEA. The study also revealed that severe lattice distortion in structure is responsible for the excellent degradation capability of HEA. Additionally, EDS analyses confirmed the occurrence of partial oxidation in the HEA during the extended mechanical alloying process (Fig. 8). These partially oxidized regions contributed to the enhanced photocatalytic behavior of HEA, undoubtedly.

In this study, HEA demonstrates the best photocatalytic performance, thus it is chosen as an example for characterization after photocatalytic testing. The XRD pattern in Fig. 15 revealed some changes in HEA's composition after photocatalytic testing. In addition to the characteristic peaks of HEA, other peaks appeared at 36.41° and 60.93°, characteristic of a $\text{ZrMo}_2\text{O}_7(\text{OH})_2$ phase according to JCPDS file (01–071–0902). During the process of photodegradation of MB by HEA, Zr^{4+} and Mo^{4+} combine with hydroxyl ions in water to produce $\text{ZrMo}_2\text{O}_7(\text{OH})_2$, which has a strong ability to adsorb MB molecules. The SEM image in Fig. 15 shows the HEA surface after photocatalytic testing,

demonstrating that the surface of the powders has slightly changed, indicating the stability of HEA morphology during MB degradation.

Furthermore, in order to assess the photocatalytic potential of the HEA and HEO materials, it is crucial to determine their semiconductor nature and flat band positions (EFB). One of the commonly employed methods for evaluating these properties involves measuring the potential dependence of the space charge region capacity (C_{sc}). In the Mott-Schottky representation (Fig. 16), variations in C_{sc} for all samples were observed concerning the applied voltage. Notably, all plotted lines exhibited a positive slope, indicating that both HEA and HEO exhibit n-type semiconductor behavior.

This finding confirms the semiconductor nature of the materials, laying the foundation for their

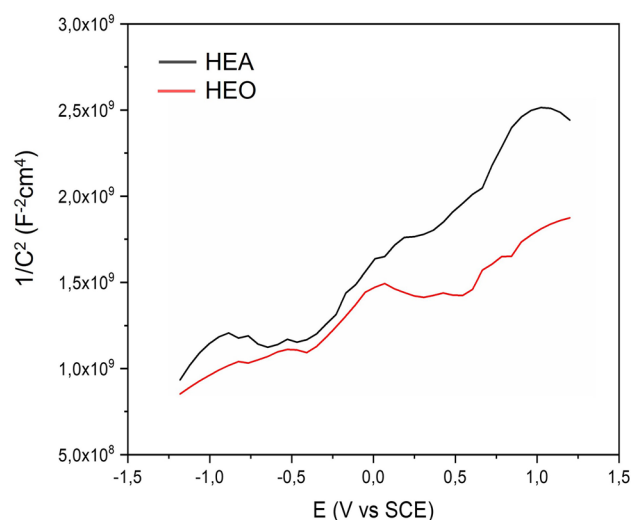


Figure 16 Mott-Schottky plots of HEA and HEO.

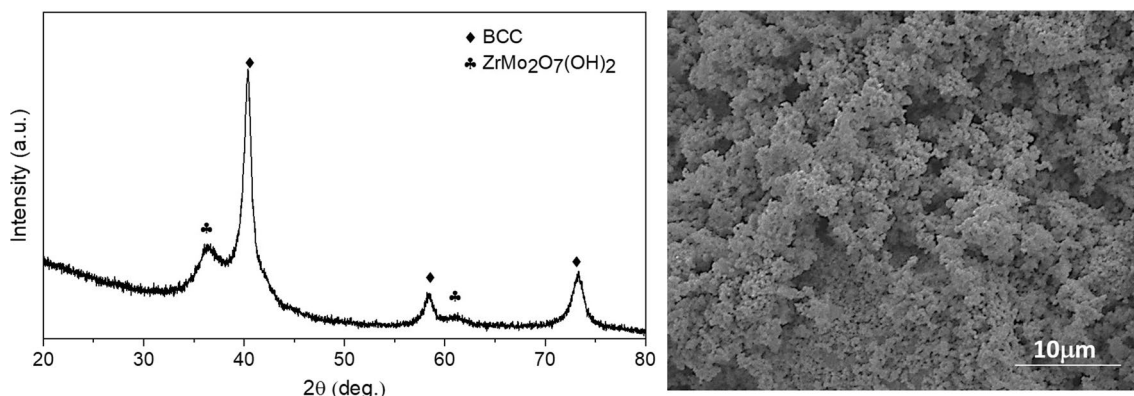


Figure 15 XRD pattern and SEM image of HEA after photocatalytic testing.

promising photocatalytic performance. In addition, this characteristic indicates their potential for efficient charge carrier separation and migration during photocatalytic processes. The observed semiconductor nature aligns with the materials' ability to harness visible light, making them suitable candidates for various applications, including solar energy conversion, water purification, and environmental remediation.

The above results show the significant potential of HEAs, exhibiting photocatalytic performance beyond the expected levels. These findings can contribute to utilizing HEA and HEO as effective photocatalysts in diverse environmental and energy-related applications. However, further detailed investigations are required to comprehend the underlying mechanisms and evaluate their application in future studies.

Conclusions

In this study, the photocatalytic performance of high entropy alloy (HEA) and its oxide counterpart, high entropy oxide (HEO), were evaluated in the degradation of methyl blue (MB) under UV irradiation. The HEA was obtained from Zr, Nb, Ta, Mo, and W particles by mechanically alloying process, and then mechano-thermal oxidized. The body-centered cubic (BCC) crystal structure is commonly observed in HEA material. In contrast to the XRD pattern of the HEA, the HEO exhibited multiple distinct crystalline peaks, indicating its diverse oxide composition. The EDS analysis revealed an oxygen atomic ratio of approximately 15% (by weight, ~ 5%) for HEA, while in the case of HEO, this ratio was significantly higher, approximately 84% (by weight, ~ 45%). The high oxidation state of all elements observed in the XPS analysis of the oxidized samples might be attributed to the process of thermal oxidation. HEA exhibited a BET surface area of $3.628 \text{ m}^2 \cdot \text{g}^{-1}$, which decreased by $1.033 \text{ m}^2 \cdot \text{g}^{-1}$ following the incorporation of the oxygen element (HEO). HEA demonstrated an average size distribution of 451.6 nm, whereas the HEO exhibited an enlarged size distribution, with an average value of 750.9 nm. The degradation results demonstrated that the HEA displayed a remarkable photodegradation performance of around 58.77%, which is approximately 1.5 times higher than that observed with the HEO. The excellent photocatalytic performance of the HEA-based material makes it a promising candidate for environmental applications,

especially in photocatalytic reactions such as methylene blue oxidation. The alloying process developed in this study is simple, and scalable, paving the way for the mass production of high-performance HEA photocatalysts with significant potential in environmental applications.

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Author contributions

O. Zakir contributed to methodology, writing—original draft—O. Guler contributed to conceptualization, resources, writing—original draft—R. Idouhli contributed to conceptualization, resources, writing—original draft—A. Nayad contributed to investigation, formal analysis—M. E. Khadiri contributed to validation, writing—review and editing—S. H. Guler contributed to validation, writing—review and editing—A. Abouelfida contributed to writing—review and editing—B. Dikici contributed to visualization, project administration, writing—original draft.

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Data availability

The data that support the findings of this study are available upon request from the authors.

Declarations

Conflict of interest The authors declare that there are no conflicts of interest.

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References

- [1] Güler SH (2023) The effect of using ferro-alloy on the properties of AlCoFeNiMoTi high-entropy alloy produced by arc-melting method: design of low cost. *Int J Met.* <https://doi.org/10.1007/s40962-023-00975-1>
- [2] Tsai M-H, Yeh J-W (2014) High-entropy alloys: a critical review. *Mater Res Lett* 2:107–123. <https://doi.org/10.1080/21663831.2014.912690>
- [3] Murty BS, Yeh JW, Ranganathan S, Bhattacharjee PP (2019) Physical metallurgy of high-entropy alloys. In: *High-Entropy Alloys*. Elsevier, pp 31–50
- [4] Yeh J-W, Chen S-K, Lin S-J et al (2004) Nanostructured high-entropy alloys with multiple principal elements: novel alloy design concepts and outcomes. *Adv Eng Mater* 6:299–303. <https://doi.org/10.1002/adem.200300567>
- [5] Yeh J-W (2006) Recent progress in high-entropy alloys. *Ann Chim Sci des Matériaux* 31:633–648. <https://doi.org/10.3166/acsm.31.633-648>
- [6] Sharma P, Dwivedi VK, Dwivedi SP (2021) Development of high entropy alloys: a review. *Mater Today Proc* 43:502–509. <https://doi.org/10.1016/j.matpr.2020.12.023>
- [7] Li W, Xie D, Li D et al (2021) Mechanical behavior of high-entropy alloys. *Prog Mater Sci* 118:100777. <https://doi.org/10.1016/j.pmatsci.2021.100777>
- [8] George EP, Curtin WA, Tasan CC (2020) High entropy alloys: a focused review of mechanical properties and deformation mechanisms. *Acta Mater* 188:435–474. <https://doi.org/10.1016/j.actamat.2019.12.015>
- [9] Poulia A, Georgatis E, Lekatou A, Karantzalis AE (2016) Microstructure and wear behavior of a refractory high entropy alloy. *Int J Refract Met Hard Mater* 57:50–63. <https://doi.org/10.1016/j.ijrmhm.2016.02.006>
- [10] Joseph J, Haghdadi N, Annasamy M et al (2020) On the enhanced wear resistance of CoCrFeMnNi high entropy alloy at intermediate temperature. *Scr Mater* 186:230–235. <https://doi.org/10.1016/j.scriptamat.2020.05.053>
- [11] Wu YD, Cai YH, Wang T et al (2014) A refractory Hf₂₅Nb₂₅Ti₂₅Zr₂₅ high-entropy alloy with excellent structural stability and tensile properties. *Mater Lett* 130:277–280. <https://doi.org/10.1016/j.matlet.2014.05.134>
- [12] Qiu Y, Thomas S, Gibson MA et al (2017) Corrosion of high entropy alloys. *npj Mater Degrad.* <https://doi.org/10.1038/s41529-017-0009-y>
- [13] Shi Y, Yang B, Liaw P (2017) Corrosion-resistant high-entropy alloys: a review. *Metals (Basel)* 7:43. <https://doi.org/10.3390/met7020043>
- [14] Wei Y, Fu Y, Pan Z et al (2021) Influencing factors and mechanism of high-temperature oxidation of high-entropy alloys: a review. *Int J Miner Metall Mater* 28:915–930. <https://doi.org/10.1007/s12613-021-2257-7>
- [15] Juan C-C, Tsai M-H, Tsai C-W et al (2015) Enhanced mechanical properties of HfMoTaTiZr and HfMoNbTaTiZr refractory high-entropy alloys. *Intermetallics* 62:76–83. <https://doi.org/10.1016/j.intermet.2015.03.013>
- [16] Akrami S, Edalati P, Fuji M, Edalati K (2021) High-entropy ceramics: review of principles, production and applications. *Mater Sci Eng R Reports* 146:100644. <https://doi.org/10.1016/j.mser.2021.100644>
- [17] Oses C, Toher C, Curtarolo S (2020) High-entropy ceramics. *Nat Rev Mater* 5:295–309. <https://doi.org/10.1038/s41578-019-0170-8>
- [18] Edalati P, Wang Q, Razavi-Khosroshahi H et al (2020) Photocatalytic hydrogen evolution on a high-entropy oxide. *J Mater Chem A* 8:3814–3821. <https://doi.org/10.1039/C9TA12846H>
- [19] Mao A, Xiang H-Z, Zhang Z-G et al (2020) A new class of spinel high-entropy oxides with controllable magnetic properties. *J Magn Magn Mater* 497:165884. <https://doi.org/10.1016/j.jmmm.2019.165884>
- [20] Zhou S, Pu Y, Zhang Q et al (2020) Microstructure and dielectric properties of high entropy Ba(Zr_{0.2}Ti_{0.2}Sn_{0.2}Hf_{0.2}Me_{0.2})O₃ perovskite oxides. *Ceram Int* 46:7430–7437. <https://doi.org/10.1016/j.ceramint.2019.11.239>
- [21] Nguyen TX, Patra J, Chang J-K, Ting J-M (2020) High entropy spinel oxide nanoparticles for superior

- lithiation–delithiation performance. *J Mater Chem A* 8:18963–18973. <https://doi.org/10.1039/D0TA04844E>
- [22] Braun JL, Rost CM, Lim M et al (2018) Charge-induced disorder controls the thermal conductivity of entropy-stabilized oxides. *Adv Mater*. <https://doi.org/10.1002/adma.201805004>
- [23] Akrami S, Murakami Y, Watanabe M et al (2022) Defective high-entropy oxide photocatalyst with high activity for CO₂ conversion. *Appl Catal B Environ* 303:120896. <https://doi.org/10.1016/j.apcatb.2021.120896>
- [24] Akrami S, Edalati P, Shundo Y et al (2022) Significant CO₂ photoreduction on a high-entropy oxynitride. *Chem Eng J* 449:137800. <https://doi.org/10.1016/j.cej.2022.137800>
- [25] Edalati P, Shen X-F, Watanabe M et al (2021) High-entropy oxynitride as a low-bandgap and stable photocatalyst for hydrogen production. *J Mater Chem A* 9:15076–15086. <https://doi.org/10.1039/D1TA03861C>
- [26] Huang T, Wu S, Jiang H et al (2020) Effect of Ti content on microstructure and properties of Ti_xZrV Nb refractory high-entropy alloys. *Int J Miner Metall Mater* 27:1318–1325. <https://doi.org/10.1007/s12613-020-2040-1>
- [27] Zhou N, Jiang S, Huang T et al (2019) Single-phase high-entropy intermetallic compounds (HEICs): bridging high-entropy alloys and ceramics. *Sci Bull* 64:856–864. <https://doi.org/10.1016/j.scib.2019.05.007>
- [28] Jia XQ, Kang L, Liu XY et al (2013) High performance ultra-thin niobium films for superconducting hot-electron devices. *IEEE Trans Appl Supercond* 23:4–8. <https://doi.org/10.1109/TASC.2012.2235508>
- [29] Liu J, Liao M, Imura M et al (2014) Low on-resistance diamond field effect transistor with high-k ZrO₂ as dielectric. *Sci Rep* 4:2–6. <https://doi.org/10.1038/srep06395>
- [30] Azdad Z, Marot L, Moser L et al (2018) Valence band behaviour of zirconium oxide, photoelectron and auger spectroscopy study. *Sci Rep* 8:1–6. <https://doi.org/10.1038/s41598-018-34570-w>
- [31] Vernickaitė E, Lelis M, Tsyntsar N et al (2020) XPS studies on the Mo oxide-based coatings electrodeposited from highly saturated acetate bath. *Chemija* 31:203–209. <https://doi.org/10.6001/CHEMIJA.V31I4.4317>
- [32] Zhang L, Wu L, Li J, Lei J (2019) Electrodeposition of amorphous molybdenum sulfide thin film for electrochemical hydrogen evolution reaction. *BMC Chem* 13:1–9. <https://doi.org/10.1186/s13065-019-0600-0>
- [33] Lee SY, Shim G, Park J, Seo H (2018) Tunable polaron-induced coloration of tungsten oxide: via a multi-step control of the physicochemical property for the detection of gaseous F. *Phys Chem Chem Phys* 20:16932–16938. <https://doi.org/10.1039/c8cp00158h>
- [34] Xie FY, Gong L, Liu X et al (2012) XPS studies on surface reduction of tungsten oxide nanowire film by Ar + bombardment. *J Electron Spectrosc Relat Phenomena* 185:112–118. <https://doi.org/10.1016/j.elspec.2012.01.004>
- [35] Zakir O, Ait Karra A, Idouhli R et al (2022) Fabrication and characterization of Ag- and Cu-doped TiO₂ nanotubes (NTs) by in situ anodization method as an efficient photocatalyst. *J Solid State Electrochem* 26:2247–2260. <https://doi.org/10.1007/s10008-022-05237-4>
- [36] Zakir O, Ait-Karra A, Idouhli R et al (2023) Effect of anodization time on the morphological, structural, electrochemical, and photocatalytic properties of anodic TiO₂ NTs. *J Solid State Chem*. <https://doi.org/10.1016/j.jssc.2023.123939>
- [37] Wang T, Wang Y, Wang N et al (2021) Development of a novel (Ni₄₀Fe₃₀Co₂₀Al₁₀)₉₀Ti₁₀ high-entropy alloy with excellent photocatalytic performance. *Mater Lett* 283:128817. <https://doi.org/10.1016/j.matlet.2020.128817>
- [38] Fu H, Quan X, Zhao H (2005) Photodegradation of γ-HCH by α-Fe₂O₃ and the influence of fulvic acid. *J Photochem Photobiol A Chem* 173:143–149. <https://doi.org/10.1016/j.jphotochem.2005.01.013>
- [39] Edalati P, Itagoe Y, Ishihara H et al (2022) Visible-light photocatalytic oxygen production on a high-entropy oxide by multiple-heterojunction introduction. *J Photochem Photobiol A Chem* 433:114167. <https://doi.org/10.1016/j.jphotochem.2022.114167>
- [40] Sun Y, Dai S (2021) High-entropy materials for catalysis: a new frontier. *Sci Adv*. <https://doi.org/10.1126/sciadv.abg1600>
- [41] Di J, Chen C, Zhu C et al (2018) Bismuth vacancy mediated single unit cell Bi₂WO₆ nanosheets for boosting photocatalytic oxygen evolution. *Appl Catal B Environ* 238:119–125. <https://doi.org/10.1016/j.apcatb.2018.06.066>

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