

Denary High-Entropy Oxide Nanoparticles Synthesized by Continuous Supercritical Hydrothermal Flow Process

Shota Hanabata,¹ Kohei Kusada,^{1,2,*} Tomokazu Yamamoto,³ Takaaki Toriyama,³ Syo Matsumura,^{3,4} Shogo Kawaguchi,⁵ Yoshiki Kubota,⁶ Yoshihide Nishida,⁷ Masaaki Haneda,⁷ and Hiroshi Kitagawa^{1,*}

¹Division of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan.

²The HAKUBI Center for Advanced Research, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan.

³The Ultramicroscopy Research Center, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan.

⁴Department of Applied Quantum Physics and Nuclear Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan.

⁵Center for Synchrotron Radiation Research, Japan Synchrotron Radiation Research Institute (JASRI), SPring-8, 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 675-5198, Japan.

⁶Department of Physics, Graduate School of Science, Osaka Metropolitan University, 1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan.

⁷Advanced Ceramics Research Center, Nagoya Institute of Technology, 10-6-29 Asahigaoka, Tajimi, Gifu 507-0071, Japan

KEYWORDS *high-entropy, oxide, nanoparticles, flow synthesis, supercritical, hydrothermal, CO oxidation, and catalysts*

ABSTRACT: High-entropy oxide nanoparticles (HEO NPs) have been intensively studied because of their attractive properties, such as high stability and enhanced catalytic activity. In this work, for the first time, denary HEO NPs were successfully synthesized by using a continuous supercritical hydrothermal flow process without calcination. Interestingly, this process allows the formation of HEO NPs on the order of seconds at a relatively lower temperature. The synthesized HEO NPs contained 10 metal elements, La, Ca, Sr, Ba, Fe, Mn, Co, Ru, Pd, and Ir, and have a perovskite-type structure. Atomic-resolution high-angle annular dark-field scanning transmission electron microscopy and energy dispersive X-ray spectroscopy measurements revealed homogeneous dispersion of the 10 metal elements. The obtained HEO NPs exhibited also a higher catalytic activity for CO oxidation reaction than the LaFeO₃ NPs.

INTRODUCTION

Recently, high-entropy materials (HEMs) have received wide attention from the scientific community due to their higher stability and enhanced properties compared with unary systems.^{1–3} In 2015, Rost et al. reported a new class of materials, namely the entropy-stabilized oxides.⁴ According to Sarker et al., high-entropy oxides (HEOs) are defined as oxides whose configurational entropy (S_{config}) is higher than $1.5R$.⁵ Recently, the entropy metric (EM) was suggested to determine the configurational entropy of materials with more complex crystal structures.⁶ With the implementation of EM, as in the previous definition of configurational entropy, a material with $EM > 1.5$ can be defined as “high entropy.”

In addition, the unique properties of nanoparticles (NPs), such as high catalytic activity due to a larger surface-to-volume ratio and unique local electronic states of the surface atoms, render them quite different from the bulk

materials. Therefore, the development of high-entropy nanomaterials can yield the fabrication of new types of materials, such as superior and highly stable catalysts.^{7,8}

Since the initial report by Rost et al., various studies on HEOs have been conducted. In the majority of these, the solid-state or sol-gel methods have been used as the synthetic method.^{9–12} The synthesis of HEMs is often performed at high-temperature conditions to leverage the large configurational entropy, which leads to larger particle sizes by the sintering process. Accordingly, the majority of the fabricated HEOs are in bulk size; in contrast, the production of HEO NPs first reported in 2019¹³ remains limited. To date, the synthesis of HEO NPs by the application of high-temperature heating using conductive carbon nanofibres¹⁴ and the implementation of the aerosol-mediated flame spray pyrolysis method¹⁵ have been reported. Although through these methods the synthesis of HEO NPs was realized by ultrafast heating, the former requires the utilization of conductive

materials and the latter emits harmful gases, such as NO_x, SO_x, and Cl₂ in pyrolyzing inorganic salts. Thus, new approaches for the synthesis of HEO NPs are urgently required to further expand the future applications of HEO NPs.

Metal oxides possess various crystal structures including rock salt, fluorite, rutile, spinel, and perovskite. Perovskite-type oxides in particular exhibit interesting physical properties, such as Li-ion conductivity,¹⁶ thermoelectric properties,¹⁷ piezoelectricity,¹⁸ ferroelectricity,¹⁹ superconductivity,²⁰ magnetism,²¹ and catalytic activities for many types of reactions including methane combustion and CO oxidation.^{22,23} The majority of the reported perovskite oxides have been synthesized by using conventional solid-phase methods,^{24–26} which accelerate the particle growth and sintering. Thus, the development of new efficient methods to synthesize perovskite-type HEO is considered of utmost importance for the fabrication of a new class of nanosized materials with enhanced physical and structural properties.

In this work, we focused on the application of a novel supercritical hydrothermal flow method using supercritical water to synthesize HEO NPs. Specifically, the flow-synthesis method has the comparative advantage that conductive materials and high temperatures are unnecessary. In addition, the flow synthesis enables control of the reagents ratio arbitrarily.²⁷ As a result, HEO NPs containing 10 metal elements, La, Ca, Sr, Ba, Fe, Mn, Co, Ru, Pd, and Ir (which were named **HEO10** NPs), were successfully synthesized at 450 °C and 30 MPa within one second. The combination of supercritical hydrothermal synthesis and flow synthesis realizes the synthesis of non-equilibrium materials because it enables particle formation immediately. The fabricated **HEO10** NPs were characterized by performing transmission electron microscopy (TEM), X-ray fluorescence (XRF), synchrotron X-ray diffraction (XRD), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and energy dispersive X-ray spectroscopy (EDS) measurements. Moreover, a CO oxidation test was conducted to thoroughly investigate the catalytic activity of the produced **HEO10** NPs. From our analysis, it was demonstrated that the **HEO10** NPs exhibit higher catalytic activity for CO oxidation than LaFeO₃ (LFO) NPs.

RESULTS AND DISCUSSION

For the synthesis of the perovskite-type HEO NPs, Goldschmidt's tolerance factor (t)²⁸ was used, which is widely employed to estimate the structural stability and distortion of perovskites. Goldschmidt's tolerance factor can be defined as follows:

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$$

Generally, a cubic perovskite is formed when $0.9 < t < 1$. For HEO NPs, r_A and r_B denote the average ionic radii of A-site and B-site cations, respectively. Here, La³⁺, Ca²⁺, Sr²⁺, and Ba²⁺ were chosen as A-site cations, with Fe³⁺, Mn²⁺, Co²⁺, Ru³⁺, Pd²⁺, and Ir³⁺ as B-site cations. When the compositions are La³⁺:Ca²⁺:Sr²⁺:Ba²⁺ = 1:1:1:1 and Fe³⁺:Mn²⁺:Co²⁺:Ru³⁺:Pd²⁺:Ir³⁺ = 15.6:15.6:15.6:1:1:1, t was calculated as 0.95, thus enabling the HEO NPs to form a cubic perovskite structure.

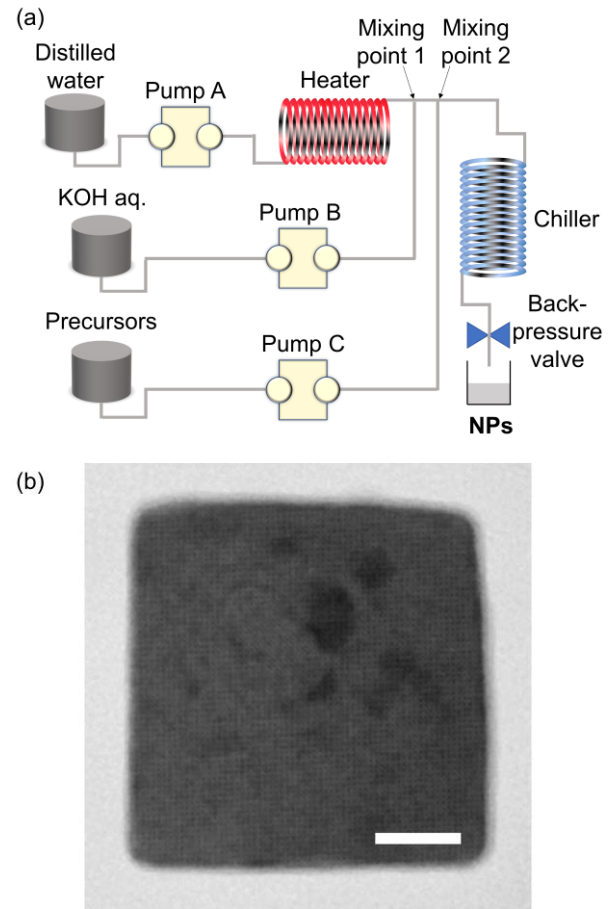


Figure 1. (a) Schematic diagram of the flow reactor. (b) STEM image of the fabricated **HEO10** NPs. The scale bar corresponds to 10 nm.

The **HEO10** NPs were synthesized by means of a supercritical hydrothermal flow-synthesis method. Supercritical water is known to be able to precipitate oxide nanoparticles.²⁹ The presence of supercritical water is important for the synthesis of oxide nanoparticles. This is because the high reaction rate and the low solubility of oxides allow the precipitation of oxide particles in supercritical water.³⁰ Furthermore, a combination of supercritical water and a flow synthesis could enable high-throughput synthesis of high-entropy oxide nanoparticles. Figure 1a shows a schematic diagram of the flow reactor used in this experiment. As observed, the reactor is equipped with a back pressure valve to realize the supercritical water reaction condition.

The precursor solution was prepared by dissolving lanthanum(III) nitrate hexahydrate, calcium nitrate tetrahydrate, strontium nitrate, barium nitrate, Iron(III) nitrate nonahydrate, manganese(II) nitrate hexahydrate, cobalt(II) nitrate hexahydrate, iridium acetate, ruthenium(III) nitrosyl nitrate solution (1.5% Ru), palladium(II) nitrate dihydrate, and nitric acid in deionized water. Note that nitric acid was added to prevent the reduction of Pd by decreasing the pH. First, deionized water was pumped at a flow rate of 80 mL/min at 30 MPa and heated to 450 °C through the electric furnace, which generated supercritical fluid. Then, both of 0.6 M KOH aqueous solution and metal precursor solution were also pumped at a flow rate of 10 mL/min. Next, the KOH solution was mixed with the supercritical water at mixing point 1, and then the metal precursor solution was injected at mixing point 2. The reactor is 1/8-inch tube (with an inner diameter of 2.17 mm) and the distance from mixing point 2 to the chiller is about 33 cm. Therefore, the volume of reaction tube from mixing point 2 to chiller is approximately 1.23 mL. Considering the total flow rate is (80+10+10) mL/min, the reaction time is estimated to be 0.7 sec at most. During the reaction, the pressure in the reactor was controlled by a back pressure valve and kept at 30 MPa. The black solution containing the product was collected at the exit. The obtained product was then washed with deionized water and ethanol, and separated by centrifugation. To determine the morphology and the particle sizes of the produced **HEO10** NPs, TEM images were obtained. The formation of some particles with a cubic shape can be seen in Figure 1b and Figure S1. The average particle size of the **HEO10** NPs was estimated to be 32.8 ± 13.6 nm by measuring the size of 100 particles (Figure S2). Also, the STEM images and the corresponding Fast Fourier Transform (FFT) patterns indicate **HEO10** NPs are crystalline perovskites (Figure S3). Additionally, the XRF measurements revealed that the **HEO10** NPs contained all 10 metal elements (Table S1).

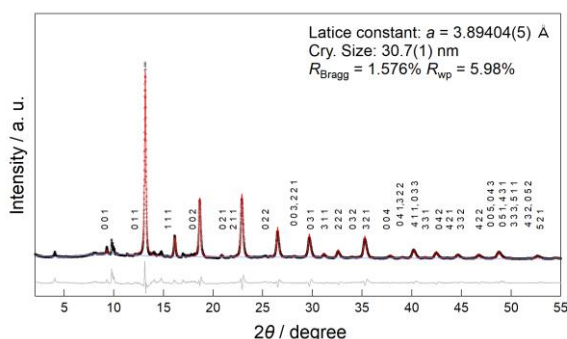


Figure 2. (black dots) The synchrotron XRD pattern of the **HEO10** NPs with (red line) Rietveld refinement, (light blue line) background, and (grey line) difference.

The crystal structure of the **HEO10** NPs was investigated by conducting synchrotron XRD measurements at the BL02B2 beamline, SPring-8. Figure 2 illustrates the synchrotron XRD pattern of the **HEO10** NPs and the results of Rietveld refinement. The profile was fitted with a single component except for minor unknown peaks that were observed in the lower angle region. This result suggested that the obtained NPs have a cubic perovskite structure with a

space group of $Pm-3m$. The lattice parameter and the average crystallite size of the **HEO10** NPs were estimated to be 3.89404(5) Å and 30.7(1) nm, respectively.

The distribution of the constituent elements of the **HEO10** NPs was also investigated by atomic-resolution HAADF-STEM EDS mapping (Figure 3). A HAADF-STEM image is depicted in Figure 3a and the corresponding EDS maps are shown in Figure 3b–l. The HAADF-STEM image was obtained from the $\langle 001 \rangle$ direction and the plane distance along the $\langle 100 \rangle$ direction was 0.39 nm, which is consistent with the result of Rietveld refinement. The maps revealed that all elements were dispersed overall. Low-magnification HAADF-STEM EDS maps are also provided in the Supporting Information (SI) to confirm the existence of low-concentration elements, such as Ir in Figure S4 and S5. The underlying reason for the low signal intensity of Co in the atomic-level EDS map can be ascribed to partial Co-rich impurity, as was clearly confirmed by the low-magnification HAADF-STEM EDS maps (Figure S4). This impurity could also be the origin of unidentified peaks in the XRD pattern. Comparing the maps for La, Ca, Sr, and Ba (Figure 3b–e) with the HAADF-STEM image (Figure 3a), these elements are located at the A-site in the perovskite structure. This is also confirmed in Figure S6a–c. These elements are overlapped with each other and occupy the same site. On the other hand, comparing the map for Fe (Figure 3f) with the maps for La and Ba (Figure 3b and 3e) and the colored composite for La and Fe (Figure S6h), we confirmed Fe is located at the B-site in the perovskite structure, different from La and so on. From Figure S6d, S6e, S6f, and S6g, Mn, Co, Ru, and Ir are located at the B-site, the same as Fe. As for Pd, it is noisy compared to Ru and Ir because it is located not only in the B-site but also in the A-site (Figure S7). In addition, considering the XRF results together, a value of 1.63 was calculated for the EM of the produced **HEO10** NPs. From this outcome, it can be argued that the **HEO10** NPs can be regarded as “high entropy” NPs. Thus, concrete evidence is presented here for the first time regarding the synthesis of **HEO10** NPs using a continuous supercritical hydrothermal flow process.

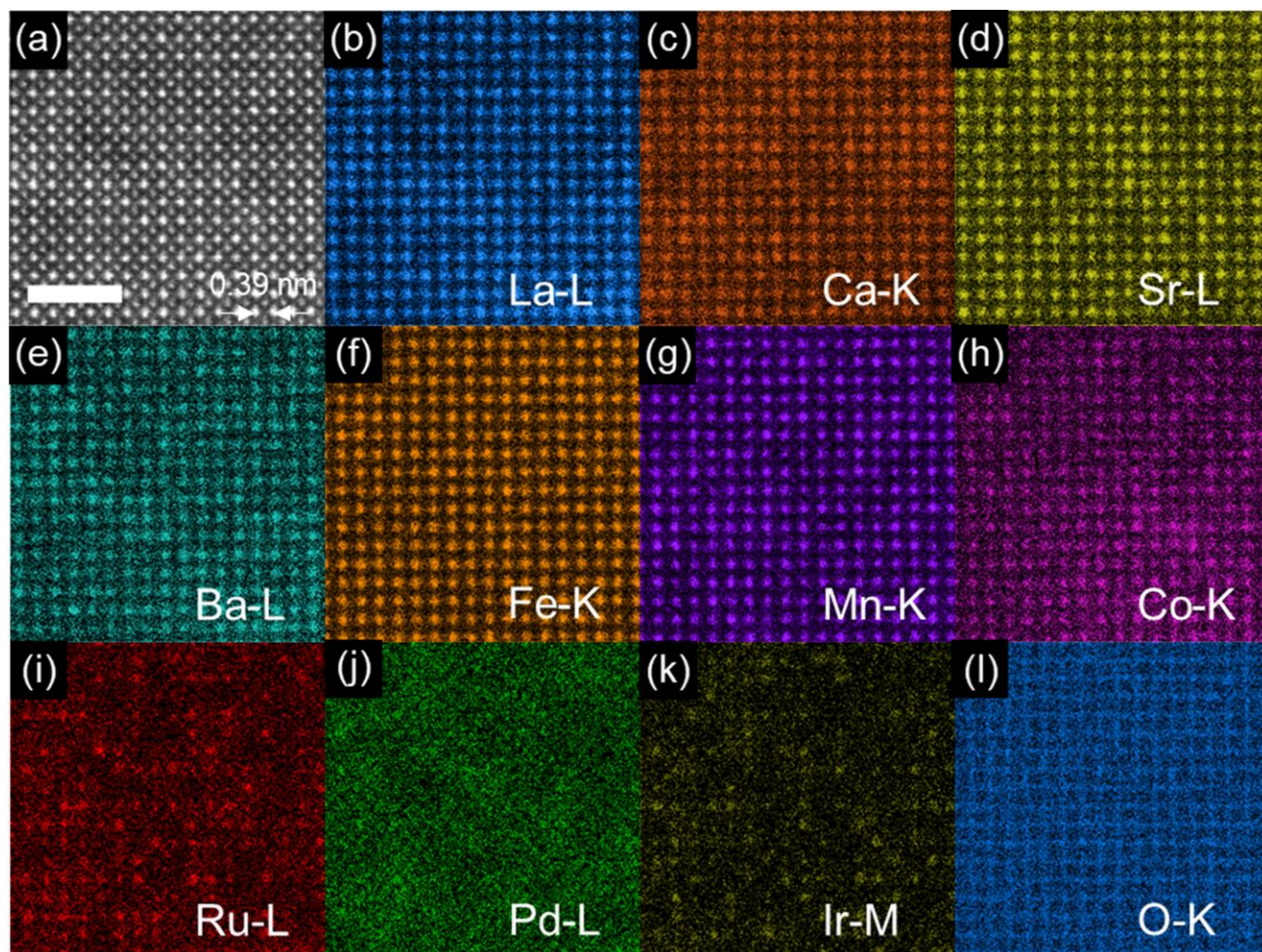


Figure 3. (a) HAADF-STEM image and (b–l) the corresponding EDS maps of **HEO10** NPs. The scale bar corresponds to 2 nm.

Furthermore, XPS analysis was conducted to determine the electronic states of the fabricated **HEO10** NPs (Figure S8). The obtained XPS spectrum of the La 3d exhibited the typical peaks of the La^{3+} compounds. According to the literature, the La 3d XPS spectrum exhibits double splitting.³¹ This effect is considered to originate from the excitation of an electron from the oxygen valence band to the lanthanum 4f level. The recorded XPS spectra of Ca 2p, Sr 3d, and Ba 3d are typical signatures of the Ca^{2+} , Sr^{2+} , and Ba^{2+} compounds. Furthermore, the Sr 3d spectrum has two sets of doublets, which are common in complex oxides containing Sr.³² According to previous reports, the complex peak shape could be attributed to a shake-up process or two different chemical environments, although the attribution of the peak shape has not been precisely determined. The spectrum of Mn 2p can also be attributed to three components of Mn^{4+} , Mn^{3+} , and satellite. The XPS spectra of Fe, Co, and Pd can be ascribed to Fe^{3+} , Co^{2+} , and Pd^{2+} , which is consistent with the valence of the precursors. The spectrum of Ru 3p has a complex shape, which may consist of Ru^{4+} and Co LMM auger peak.³³ The spectrum of Ir 4f is composed of two components, which are believed to be derived from Ir^{4+} and the shake-up satellites.³⁴ Given the valences and compositions of cations, it is considered that **HEO10** NPs contain a certain amount of oxygen vacancies. The amount of oxygen vacancy

was estimated to be $\text{ABO}_{2.7}$ by Rietveld refinement of the XRD pattern.

To demonstrate the catalytic properties of **HEO10** NPs, a CO oxidation test was also conducted by using a quartz tubular reactor. Figure 4 shows the temperature dependence of CO conversion of the **HEO10** NPs and LFO NPs. LFO

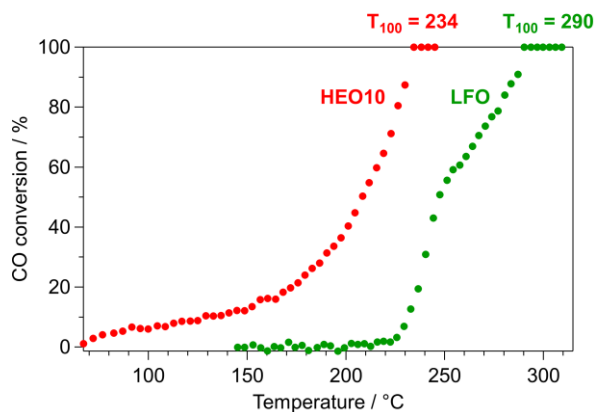


Figure 4. CO conversion curves of **HEO10** NPs (red) and LFO (green) NPs

NPs were prepared in the same way as the control experiment (Figures S9 and S10, Table S2). Figure 4 shows that 100% CO conversion was achieved at 234 °C for **HEO10** NPs and at 290 °C for LFO NPs, demonstrating that **HEO10** NPs have a higher catalytic activity than LFO NPs. In particular, the light-off temperature of **HEO10** NPs was 80 °C lower than that of LFO NPs. The high catalytic activity of the **HEO10** NPs was reproduced in the second cycle (Figure S11). We note that **HEO10** NPs contains a small amount of impurities and the possibility of impurity effect on catalytic activity cannot be completely excluded.

The multiple inflection points exist in the CO conversion curves. To identify the origin of these inflection points, CO oxidation with $^{18}\text{O}_2$ for **HEO10** NPs and LFO NPs was conducted. Figure 5 shows the mass spectra of $\text{CO}+^{18}\text{O}_2$ reaction for HEO NPs and LFO NPs. As shown in Figure 5, C^{16}O_2 , which is generated using the oxygen in the perovskite lattices, was detected from 50 °C for **HEO10** NPs and from 100 °C for LFO NPs. Subsequently, for **HEO10** NPs, the ratio of $\text{C}^{16}\text{O}^{18}\text{O}$, which is generated using the fed oxygen, became higher than that of C^{16}O_2 at the temperature just before the CO conversion reached 100%. On the other hand, for LFO NPs, the reversal of the ratios of C^{16}O_2 and $\text{C}^{16}\text{O}^{18}\text{O}$ occurred at a lower temperature than the temperature where CO conversion reached 100%. Furthermore, Figure S12 shows the

overlay of the signal intensity of CO_2 and O_2 detected by micro gas chromatograph on the CO conversion curves. For both **HEO10** NPs and LFO NPs, the CO conversion curves almost overlap with the quantitative value curve for CO_2 , indicating that almost all of the CO fed into the reactor was converted into CO_2 . On the other hand, O_2 fed into the reactor was not consumed much at lower temperatures for **HEO10** NPs and LFO NPs, although it was consumed at higher temperatures for both samples. These results support that the lattice oxygen in the perovskite contributes to the reaction at low temperatures and the driving temperature is much lower for **HEO10** NPs than LFO NPs. Therefore, it is concluded that the origin of the inflection points is the difference in the oxygen sources and the enhanced catalytic activity of **HEO10** NPs would be attributed to the high lattice oxygen activity in **HEO10** NPs.

CONCLUSION

In conclusion, perovskite-type denary HEO NPs consisting of largely different s-, d-, and f-block elements on the periodic table of the elements were successfully synthesized using the new method of supercritical hydrothermal flow reaction. With the implementation of this method, the composition of the produced HEO NPs could be easily controlled by the ratio of the reagents. Additionally, a flow synthesis would enable high-throughput synthesis of HEO NPs in the future. Moreover, the synthesized HEO NPs showed higher catalytic activity of CO oxidation than LFO NPs. Our work paves the way for the development of a variety of HEO NPs using widely available elements.

EXPERIMENTAL SECTION

Synthesis of HEO10 NPs. **HEO10** NPs were synthesized by using a supercritical hydrothermal flow-synthesis method. The precursor solution of **HEO10** NPs was prepared by dissolving 2.0 mmol of lanthanum(III) nitrate hexahydrate, 2.0 mmol of calcium nitrate tetrahydrate, 2.0 mmol of strontium nitrate, 2.0 mmol of barium nitrate, 2.5 mmol of Iron(III) nitrate nonahydrate, 2.5 mmol of manganese(II) nitrate hexahydrate, 2.5 mmol of cobalt(II) nitrate hexahydrate, 0.16 mmol of iridium acetate, ruthenium(III) nitrosyl nitrate solution (1.5% Ru) corresponding to 0.16 mmol Ru, 0.16 mmol of palladium(II) nitrate dihydrate, and 1 mL of nitric acid in 160 mL of water. First, deionized water was pumped at a flow rate of 80 mL/min at 30 MPa and heated to 450 °C through the electric furnace, which generated supercritical fluid. Then, both of 0.6 M KOH aqueous solution and metal precursor solution were also pumped at a flow rate of 10 mL/min. Next, the KOH solution was mixed with the supercritical water at mixing point 1, and then the metal precursor solution was injected at mixing point 2. The reactor is 1/8-inch tube (with an inner diameter of 2.17 mm) and the distance from mixing point 2 to the chiller is about 33 cm. Therefore, the volume of reaction tube from mixing point 2 to chiller is approximately 1.23 mL. Considering the total flow rate is (80+10+10) mL/min, the reaction time is estimated to be 0.7 sec at most. During the reaction, the pressure in the reactor was controlled by a back pressure valve and kept at 30 MPa. The black solution containing the product was collected at the exit. The obtained product was

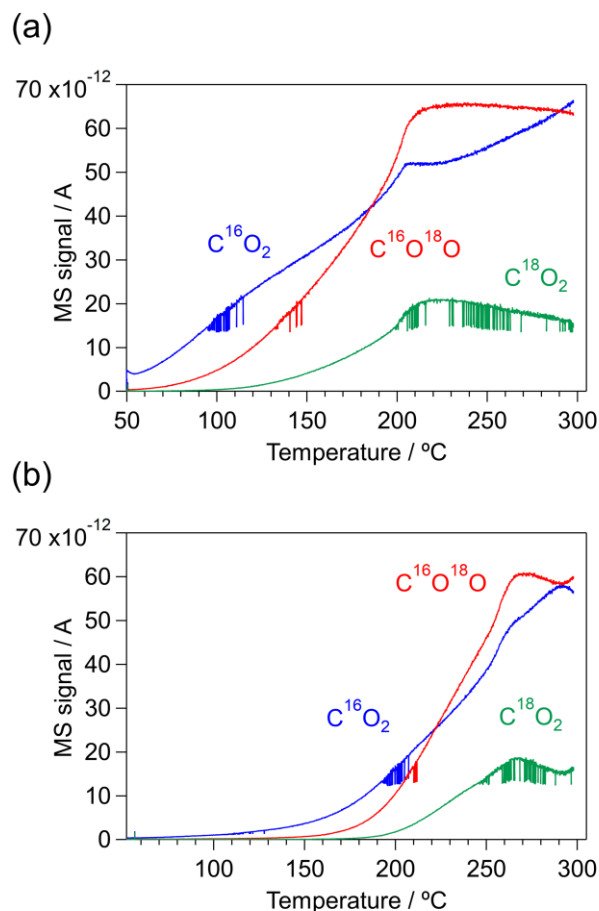


Figure 5. Mass spectra of $\text{CO}+^{18}\text{O}_2$ reaction for (a) **HEO10** NPs and (b) LFO NPs.

then washed with deionized water and ethanol, and separated by centrifugation.

Characterization of HEO10 NPs. The appearance of the HEO10 NPs was observed by TEM using a Hitachi HT7700 instrument operated at 100 kV. The crystal structure of the produced HEO10 NPs was characterized by capillary synchrotron XRD analysis measured at the BL02B2 beamline at SPring-8. The XRD patterns of the samples sealed in a glass capillary were measured with a wavelength of 0.6301 Å. The Rietveld refinement was performed with the program TOPAS 3.0 (Bruker AXS). For the profile refinement, the Pearson VII function was used. The contribution to the peak shape because of the experimental setup was obtained after performing a Rietveld refinement of the CeO₂ standard. High-resolution scanning transmission electron microscope (HRSTEM) images and STEM-EDS mapping data were obtained on a JEOL ARM 200CF STEM instrument operated at 200 kV and JEOL JEM-ARM300F2 STEM instrument operated at 200 kV. STEM-EDS mappings were obtained for La-L, Ca-K, Sr-L, Ba-L, Fe-K, Co-K, Mn-K, Ru-L, Pd-L, and Ir-M with net count processing to avoid overestimation due to the overlap of peaks.

CO oxidation test. The catalytic activity of the HEO10 NPs was evaluated in a quartz tubular reactor ($\varnothing = 10$ mm). Initially, 50 mg of HEO10 NPs was placed between two quartz wool layers. The feed gas consisting of 10% CO, 10% O₂, and 80% He was passed at a total flow rate of 100 mL/min, and controlled by a gas mixer. The outlet gas was analyzed by micro gas chromatography. The temperature of the reactor was heated at the rate of 1 °C/min by an electric heater. The CO conversion was calculated by $(c_1 - c_2)/c_1 \times 100\%$, where c_1 is the CO concentration at 50 °C (0% CO conversion), and c_2 refers to the CO concentration at that temperature.

CO oxidation with ¹⁸O₂. To identify oxygen species, which participates in CO oxidation over HEO10 NPs and LFO NPs, CO oxidation with ¹⁸O₂ was performed with a fixed-bed flow reactor system. A reaction gas mixture containing CO (0.1%) and ¹⁸O₂ (0.1%) diluted with He as the balance gas was fed through a catalyst (10 mg), pretreated in situ in a flow of 5% O₂/He at 200 °C for 30 min, at a rate of 20 cm³ min⁻¹. The reaction temperature was linearly raised from 50 °C to 300 °C at a rate of 10 °C min⁻¹. The effluent gas from the reactor was continuously monitored by a quadrupole mass spectrometer (PFEFFER OminiStar) for CO ($m/e = 28$) and the isotopic molecules of CO₂ (C¹⁶O₂ ($m/e = 44$), C¹⁶O¹⁸O ($m/e = 46$) and C¹⁸O₂ ($m/e = 48$)).

ASSOCIATED CONTENT

This Supporting Information is available free of charge at <http://pubs.acs.org/doi/> Materials and experimental details, TEM, STEM-EDS, XPS spectra, CO oxidation test data, and Tables (PDF)

AUTHOR INFORMATION

Corresponding Authors

Kohei Kusada - *The HAKUBI Center for Advanced Research, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan*; orcid.org/0000-0002-9679-6749; E-mail: kusada@kuchem.kyoto-u.ac.jp

Hiroshi Kitagawa - *Division of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan*; orcid.org/0000-0001-6955-3015; E-mail: kita-gawa@kuchem.kyoto-u.ac.jp

Authors

Shota Hanabata - *Division of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan*;

Tomokazu Yamamoto - *The Ultramicroscopy Research Center, Kyusyu University, Fukuoka 819-0395, Japan*

Takaaki Toriyama - *The Ultramicroscopy Research Center, Kyusyu University, Fukuoka 819-0395, Japan*

Syo Matsumura - *Department of Applied Quantum Physics and Nuclear Engineering and The Ultramicroscopy Research Center, Kyusyu University, Fukuoka 819-0395, Japan*; Present Address: *National Institute of Technology, Kurume College, 1-1-1 Komorino, Kurume-shi, Fukuoka 830-8555, Japan*

Shogo Kawaguchi - *Research & Utilization Division, Japan Synchrotron Radiation Research Institute (JASRI), Spring-8, Hyogo 679-5198, Japan*

Yoshiki Kubota - *Department of Physics, Graduate School of Science, Osaka Metropolitan University, Osaka 599-8531, Japan*.

Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

We acknowledge the support from a Grant-in-Aid for Specially Promoted Research, No. 20H05623 and a Grant-in-Aid for Scientific Research (B), No. 21H01762, and JST PRESTO JPMJPR20A3. Synchrotron XRD measurements were carried out at beamline BL02B2 at SPring-8 under proposal Nos. 2022A1373.

REFERENCES

- (1) Tsai, M.-H.; Yeh, J.-W. High-Entropy Alloys: A Critical Review. *Mater. Res. Lett.* **2014**, *2*, 107–123.
- (2) Sarkar, A.; Wang, Q.; Schiele, A.; Chellali, M. R.; Bhattacharya, S. S.; Wang, D.; Brezesinski, T.; Hahn, H.; Velasco, L.; Breitung, B. High-Entropy Oxides: Fundamental Aspects and Electrochemical Properties. *Adv. Mater.* **2019**, *31*, e1806236.
- (3) Amiri, A.; Shahbazian-Yassar, R. Recent Progress of High-Entropy Materials for Energy Storage and Conversion. *J. Mater. Chem. A* **2021**, *9* (2), 782–823.
- (4) Rost, C. M.; Sachet, E.; Borman, T.; Moballeghe, A.; Dickey, E. C.; Hou, D.; Jones, J. L.; Curtarolo, S.; Maria, J.-P. Entropy-Stabilized Oxides. *Nat. Commun.* **2015**, *6* (1), 1–8.
- (5) Sarkar, A.; Breitung, B.; Hahn, H. High Entropy Oxides: The Role of Entropy, Enthalpy and Synergy. *Scr. Mater.* **2020**, *187*, 43–48.
- (6) Dippo, O. F.; Vecchio, K. S. A Universal Configurational Entropy Metric for High-Entropy Materials. *Scr. Mater.* **2021**, *201*, 113974.
- (7) Yao, Y.; Dong, Q.; Brozena, A.; Luo, J.; Miao, J.; Chi, M.; Wang, C.; Kevrekidis, I. G.; Ren, Z. J.; Greeley, J.; Wang, G.; Anapolsky, A.; Hu, L. High-Entropy Nanoparticles: Synthesis-Structure-Property Relationships and Data-Driven Discovery. *Science* **2022**, *376*, eabn3103.

- (8) Kusada, K.; Mukoyoshi, M.; Wu, D.; Kitagawa, H. Chemical Synthesis, Characterization, and Properties of Multi-Element Nanoparticles. *Angew. Chem. Int. Ed Engl.* **2022**, *61* (48), e202209616.
- (9) Dąbrowa, J.; Stygar, M.; Mikuła, A.; Knapik, A.; Mroczka, K.; Tejchman, W.; Danielewski, M.; Martin, M. Synthesis and Microstructure of the $(\text{Co,Cr,Fe,Mn,Ni})_3\text{O}_4$ High Entropy Oxide Characterized by Spinel Structure. *Mater. Lett.* **2018**, *216*, 32–36.
- (10) Teng, Z.; Tan, Y.; Zeng, S.; Meng, Y.; Chen, C.; Han, X.; Zhang, H. Preparation and Phase Evolution of High-Entropy Oxides $\text{A}_2\text{B}_2\text{O}_7$ with Multiple Elements at A and B Sites. *J. Eur. Ceram. Soc.* **2021**, *41* (6), 3614–3620.
- (11) Asim, M.; Hussain, A.; Khan, S.; Arshad, J.; Butt, T. M.; Hana, A.; Munawar, M.; Saira, F.; Rani, M.; Mahmood, A.; Janjua, N. K. Sol-Gel Synthesized High Entropy Metal Oxides as High-Performance Catalysts for Electrochemical Water Oxidation. *Molecules* **2022**, *27* (18). <https://doi.org/10.3390/molecules27185951>.
- (12) Liu, J.; Ma, C.; Wang, L.; Ren, K.; Ran, H.; Feng, D.; Du, H.; Wang, Y. Single-Phase Formation Mechanism and Dielectric Properties of Sol-Gel-Derived $\text{Ba}(\text{Ti}_{0.2}\text{Zr}_{0.2}\text{Sn}_{0.2}\text{Hf}_{0.2}\text{Ce}_{0.2})\text{O}_3$ High-Entropy Ceramics. *J. Mater. Sci. Technol.* **2022**, *130*, 103–111.
- (13) Qiu, N.; Chen, H.; Yang, Z.; Sun, S.; Wang, Y.; Cui, Y. A High Entropy Oxide $(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{O})$ with Superior Lithium Storage Performance. *J. Alloys Compd.* **2019**, *777*, 767–774.
- (14) Li, T.; Yao, Y.; Huang, Z.; Xie, P.; Liu, Z.; Yang, M.; Gao, J.; Zeng, K.; Brozena, A. H.; Pastel, G.; Jiao, M.; Dong, Q.; Dai, J.; Li, S.; Zong, H.; Chi, M.; Luo, J.; Mo, Y.; Wang, G.; Wang, C.; Shahbazian-Yassar, R.; Hu, L. Denary Oxide Nanoparticles as Highly Stable Catalysts for Methane Combustion. *Nat. Catal.* **2021**, *4* (1), 62–70.
- (15) Phakatkar, A. H.; Saray, M. T.; Rasul, M. G.; Sorokina, L. V.; Ritter, T. G.; Shokuhfar, T.; Shahbazian-Yassar, R. Ultrafast Synthesis of High Entropy Oxide Nanoparticles by Flame Spray Pyrolysis. *Langmuir* **2021**, *37* (30), 9059–9068.
- (16) Huang, B.; Xu, B.; Li, Y.; Zhou, W.; You, Y.; Zhong, S.; Wang, C.-A.; Goodenough, J. B. Li-Ion Conduction and Stability of Perovskite $\text{Li}_{3/8}\text{Sr}_{7/16}\text{Hf}_{1/4}\text{Ta}_{3/4}\text{O}_3$. *ACS Appl. Mater. Interfaces* **2016**, *8* (23), 14552–14557.
- (17) Yasukawa, M.; Kono, T.; Ueda, K.; Yanagi, H.; Wng Kim, S.; Hosono, H. Thermoelectric Properties and Figure of Merit of Perovskite-Type $\text{Ba}_{1-x}\text{La}_x\text{SnO}_3$ with $x=0.002\text{--}0.008$. *Solid State Commun.* **2013**, *172*, 49–53.
- (18) Shi, C.; Ma, J.-J.; Jiang, J.-Y.; Hua, M.-M.; Xu, Q.; Yu, H.; Zhang, Y.; Ye, H.-Y. Large Piezoelectric Response in Hybrid Rare-Earth Double Perovskite Relaxor Ferroelectrics. *J. Am. Chem. Soc.* **2020**, *142* (21), 9634–9641.
- (19) von Hippel, A. Ferroelectricity, Domain Structure, and Phase Transitions of Barium Titanate. *Rev. Mod. Phys.* **1950**, *22* (3), 221–237.
- (20) Rubel, M. H. K.; Takei, T.; Kumada, N.; Ali, M. M.; Miura, A.; Tadanaga, K.; Oka, K.; Azuma, M.; Magome, E.; Moriyoshi, C.; Kuroiwa, Y. Hydrothermal Synthesis, Structure, and Superconductivity of Simple Cubic Perovskite $(\text{Ba}_{0.62}\text{K}_{0.38})(\text{Bi}_{0.92}\text{Mg}_{0.08})\text{O}_3$ with $T_c \sim 30$ K. *Inorg. Chem.* **2017**, *56* (6), 3174–3181.
- (21) Nguyen, L. T.; Saubanère, M.; Zhang, Q.; Cava, R. J. Structure, Magnetism, and First-Principles Modeling of the $\text{Na}_{0.5}\text{La}_{0.5}\text{RuO}_3$ Perovskite. *Chem. Mater.* **2021**, *33* (2), 600–607.
- (22) Bashan, V.; Ust, Y. Perovskite Catalysts for Methane Combustion: Applications, Design, Effects for Reactivity and Partial Oxidation. *Int. J. Energy Res.* **2019**, No. er.4721. <https://doi.org/10.1002/er.4721>.
- (23) Gholizadeh, A. $\text{La}_{1-x}\text{Ca}_x\text{Co}_{1-y}\text{Mg}_y\text{O}_3$ Nano-Perovskites as CO Oxidation Catalysts: Structural and Catalytic Properties. *J. Am. Ceram. Soc.* **2017**, *100* (3), 859–866.
- (24) Wang, D.; Jiang, S.; Duan, C.; Mao, J.; Dong, Y.; Dong, K.; Wang, Z.; Luo, S.; Liu, Y.; Qi, X. Spinel-Structured High Entropy Oxide $(\text{FeCoNiCrMn})_3\text{O}_4$ as Anode towards Superior Lithium Storage Performance. *J. Alloys Compd.* **2020**, *844*, 156158.
- (25) Qiu, N.; Chen, H.; Yang, Z.; Sun, S.; Wang, Y.; Cui, Y. A High Entropy Oxide $(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2}\text{O})$ with Superior Lithium Storage Performance. *J. Alloys Compd.* **2019**, *777*, 767–774.
- (26) Lun, Z.; Ouyang, B.; Kwon, D.-H.; Ha, Y.; Foley, E. E.; Huang, T.-Y.; Cai, Z.; Kim, H.; Balasubramanian, M.; Sun, Y.; Huang, J.; Tian, Y.; Kim, H.; McCloskey, B. D.; Yang, W.; Clément, R. J.; Ji, H.; Ceder, G. Cation-Disordered Rocksalt-Type High-Entropy Cathodes for Li-Ion Batteries. *Nat. Mater.* **2021**, *20* (2), 214–221.
- (27) Kusada, K.; Kitagawa, H. Continuous-Flow Syntheses of Alloy Nanoparticles. *Mater. Horiz.* **2022**, *9* (2), 547–558.
- (28) Goldschmidt, V. M. Die Gesetze der Krystallochemie. *Naturwissenschaften* **1926**, *14* (21), 477–485.
- (29) Adschiri, T.; Hakuta, Y.; Sue, K.; Arai, K. Hydrothermal Synthesis of Metal Oxide Nanoparticles at Supercritical Conditions. *J. Nanopart. Res.* **2001**, *3* (2), 227–235.
- (30) Abe, Y.; Satou, I.; Aida, T.; Adschiri, T. Formation of La-Based Perovskite Compounds in Supercritical Water. *Ceram. Int.* **2018**, *44* (11), 12996–13003.
- (31) Lam, D. J.; Veal, B. W.; Ellis, D. E. Electronic Structure of Lanthanum Perovskites with 3d Transition Elements. *Phys. Rev. B Condens. Matter* **1980**, *22* (12), 5730–5739.
- (32) Vovk, G.; Chen, X.; Mims, C. A. In Situ XPS Studies of Perovskite Oxide Surfaces under Electrochemical Polarization. *J. Phys. Chem. B* **2005**, *109* (6), 2445–2454.
- (33) Bekermann, D.; Gasparotto, A.; Barreca, D.; Devi, A.; Fischer, R. A. $\text{P-Co}_3\text{O}_4/\text{n-ZnO}$, Obtained by PECVD, Analyzed by X-Ray Photoelectron Spectroscopy. *Surf. Sci. Spectra* **2011**, *18* (1), 36–45.
- (34) Chen, Y.; Li, H.; Wang, J.; Du, Y.; Xi, S.; Sun, Y.; Sherburne, M.; Ager, J. W., 3rd; Fisher, A. C.; Xu, Z. J. Exceptionally Active Iridium Evolved from a Pseudo-Cubic Perovskite for Oxygen Evolution in Acid. *Nat. Commun.* **2019**, *10* (1), 572.

